



Saskatchewan
Ministry of
Agriculture



RESEARCH

FINAL REPORT

ADF

AGRICULTURE

DEVELOPMENT

FUND

20080154

**PYROLYSIS OF AGRICULTURE AND LIVESTOCK
RESIDUE**

Funded by: The Agriculture Development Fund

July 2011

Prepared by: Saskatchewan Research Council

CONFIDENTIAL FINAL REPORT

Pyrolysis of Agricultural and Livestock Residues

By E. Powell
D. Anweiler
G. Vlajnic
Z. Wang

Saskatchewan Research Council
Agriculture, Biotechnology & Food

SRC Publication No. 12673-1C11

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EXECUTIVE SUMMARY

Motivation / Conclusions / Recommendations

The research objective of this project was to assess mobile pyrolysis technology as a novel solution for managing agricultural and livestock residues. The results provide the information required to more accurately assess the economics of the application of this technology utilizing agricultural residues. A novel mobile pyrolysis unit was evaluated to determine its mobility, robustness, and efficiency for utilization of various agricultural feedstocks, specifically wheat straw, poultry litter, and flax shives. This was done through the characterization of products and their potential value, in combination with an assessment of the capital cost and operating costs for the pyrolysis technology. The amount of agricultural residues within Saskatchewan is extensive, and their value has significant opportunity for growth. This project assessed the technology for commercial potential at scales varying from small scale to larger operations. In addition, the potential demonstrated in this work for integration extends the commercial opportunities. Lastly, these residues may provide the resource that is essential for the production of many different value-added chemicals, which include cellulosic ethanol and fertilizers, all of which are in high demand. ABRI Tech Inc. (Ottawa, ON, Canada) is the technology provider in this project.

The benefits to the Saskatchewan agricultural industry of this technology and research are directly associated with the ability to increase the value of residues from primary and secondary production. The products that may be generated, fertilizers and fuels specifically, also have the potential to offset the primary input costs to agricultural and livestock producers, making development of this technology attractive for primary producers in Saskatchewan. The products also have the economic potential to be critical feedstocks for further downstream processing. Yet another opportunity for economic potential is that the technology under investigation is extremely flexible in scale as a result of the various commercial sizes available, and furthermore it is mobile and so may be utilized at various sites on a routine schedule.

This project has the potential to reduce costs for production, increase the value of residues, provide a novel solution for agricultural and livestock residue management, and reduce our dependence on fossil fuels and the associated impact on environment.

Pyrolysis products are feedstock dependent as well as highly dependent on the technology and the operating conditions. Pyrolysis oil and char were characterized in such a way that

their value in various end-uses could be assessed. For oil used as a combustion fuel, straw-based oils have the highest heating values. The superior pyrolysis oil for upgrading is that produced from poultry litter at high temperature, due to its lower oxygen content and acidity. The best char for use as fuel are those from flax shive produced at high temperature, with all being suitable as soil amendments. The interactions that exist between the technology, feedstocks, and operating conditions must be optimized in order to develop the operating procedures and instructions for yielding a product with consistent characteristics.

Detailed Project Task Summary

In Task 1, Planning and Identification of University of Saskatchewan (U of S) Resources, a series of meetings were conducted to identify the resources required to conduct this work, the working relationship between the organizations involved, management of intellectual property, and the responsibilities of the collaborators in the completion of the activities.

In Task 2, Prioritization of Agricultural Feedstocks, a prioritization matrix was developed to identify which agricultural and livestock residues should be assessed as part of this study.

There are many different agricultural residues that may be utilized for assessing the value of pyrolysis technology. The prioritization matrix developed will include key drivers from the agricultural industry, fit to technology, feedstock volume, feedstock collection, and potential for high value end-use. This prioritization identified a short list of four agricultural and livestock feedstocks for subsequent assessment: flax straw, wheat straw, poultry litter, and dried distiller's grain with soluble (DDGS). The last of these was found to be unsuitable for the present study.

In Task 3, Commissioning of Mobile Pyrolysis Unit, the acquisition, installation in a suitable facility, and commissioning of the pyrolysis unit was undertaken by the Saskatchewan Research Council (SRC). This task also included troubleshooting the pyrolysis unit design and modifications for use with the selected pyrolysis feedstocks.

Task 3 was not strictly part of the project funded by the Agriculture Development Fund (ADF), but was in fact an in-kind activity by SRC undertaken prior to the start of the pyrolysis study. An ABRI-Tech unit was purchased by SRC, and was commissioned over several months of work, including extensive modification and adaptation for mobile use on a trailer and outdoors.

In Task 4, Establishment of Baseline of Pyrolysis Technology, a baseline of operation was determined with which the pyrolysis technology was assessed.

A baseline provides a standard or known value to which the experimental results are compared when assessed. The baseline was established using mixed hardwood sawdust as the feedstock and was critical to ensuring the results are consistent and repeatable.

In Task 5, Pyrolysis of Agricultural Feedstocks, the pyrolysis of the identified feedstocks from Task 2 was undertaken.

The pyrolysis involved performing multiple runs at different operating conditions, which allowed production to be oriented towards char, oil, or gas as the primary product. Operating techniques also needed to be developed to manage varying feedstock characteristics.

In Task 6, Characterization of Pyrolysis Products, the obtained pyrolysis products – oil, char, and gas – were characterized based on composition and properties in such a way that an assessment could be made of the applicability of these products for various end-uses.

The pyrolysis oils were characterized to identify their value as a fuel with characteristics that are suited to be utilized directly for energy or as an intermediate for subsequent conversion into bio-gasoline or bio-diesel. The pyrolysis char was characterized as a soil amendment, a bio-fertilizer, an intermediate for subsequent processing, and as an additive to increase the calorific value of the pyrolysis oil.

In Task 7, Assessment of Applicability of Pyrolysis for Specific End-Uses, the pyrolysis product characterization data was used to determine the value of these products in particular end-uses, as well as for use as a feedstock for additional value-added processing.

In Task 8, Confirmation of Business Case for Commercialization, recommendations were developed and provided based on the use of this technology in commercial applications at various scales of operation. An economic evaluation assists in gaining an overall understanding of the economics associated with the utilization of mobile pyrolysis technology in the agricultural industry.

In Task 9, Project Management and Final Reporting and Submission, all tasks required for the project, both by SRC and the U of S, were managed; a final report for the entire project, including all of the previous tasks, was completed; and all required submissions to ADF were undertaken.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the Saskatchewan Agriculture Development Fund (ADF), and the patience and understanding extended by Chris Smith and Shawn Gibson of the Saskatchewan Ministry of Agriculture for completing this project. We also acknowledge the generous donation of feedstocks by several parties. The wheat and flax straw and flax shive were provided by Mark Stumborg, Agriculture and Agri-Food Canada. The poultry litter was donated by Advanced Poultry Technologies Inc. North West Bio-Energy provided the wheat DDGS.

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BACKGROUND

The research objective of this project was to assess mobile pyrolysis technology as a novel solution for managing agricultural and livestock residues. The results provide the information required to more accurately assess the economics of the application of this technology utilizing agricultural residues. The study involved the characterization of products and their potential value, in combination with an assessment of the capital cost and operating costs for the pyrolysis technology.

SRC has conducted studies on the utilization of pyrolysis technologies for the energy densification of agricultural and forestry feedstocks. SRC has also investigated the utilization of pyrolysis products as intermediates for downstream conversion into fuels and fertilizers. A low cost, low parasitic load, mobile technology has the potential to provide a solution to the barriers that have hindered other technologies. SRC has also investigated downstream upgrading technologies for conversion of pyrolysis products into higher value products. This research expanded SRC's capabilities and provided a venue for pilot demonstration of technology.

The amount of agricultural residues within Saskatchewan is extensive and their value has significant opportunity for growth. This project assessed the technology for commercial potential at scales which vary from small scale operation to larger operations. In addition, the potential demonstrated in this work for forestry residues to be integrated into the application of the technology extends the commercial opportunities. Lastly, these residues may provide the resource that is essential for the production of many different value-added chemicals, which include cellulosic ethanol and fertilizers, all of which are in high demand. ABRI-Tech Inc., a pioneer of mobile pyrolysis technology, is the technology provider in this project.

The novel mobile pyrolysis technology was assessed to determine the mobility, robustness, and efficiency for utilization of various agricultural feedstocks. Pyrolysis products are feedstock dependant as well as highly dependant on the technology and the operating conditions. Pyrolysis oil and char was characterized in a way that their value in various end-uses could be assessed. An effort was started to optimize the interactions that exist between technology, feedstocks, and operating conditions in order to develop the operating procedures and instructions for yielding a product with consistent characteristics. This optimization will take further work.

The benefits to the Saskatchewan agricultural industry are directly associated with the ability to increase the value of residues from primary and secondary production. The products that may be produced, fertilizers and fuels specifically, also have the potential to leverage the input costs to primary production. The products also have the economic potential to be critical feedstocks for further downstream processing. Yet another opportunity for economic potential is that the technology under investigation is extremely flexible in scale as a result of the various commercial sizes available, and furthermore it is mobile and so may be utilized at various sites on a routine schedule.

This project demonstrated the potential to reduce costs for production, increase the value of residues, provide a novel solution for agricultural and livestock residue management, and reduce our dependence on fossil fuels and the associated impact on environment. As well, it further strengthened the collaboration between SRC and the U of S in improving the economic potential of the Saskatchewan agriculture industry through implementation of thermal processing technologies.

1. LITERATURE SURVEY

1.1 Introduction

As Saskatchewan's bioenergy sector continues to grow, researchers continue to look for innovative methods to create biofuels from wastes. The available biomass of the world is 220 billion metric tonnes (dry basis) per year (Naik et al., 2009) and increasing the capacity of energy from biomass reduces the fossil fuel consumption. Agricultural residues are abundant throughout the Prairie provinces. Saskatchewan alone has 15 million hectares of cropped farmland, with the major crop being wheat, whose grains leave straw on the field during harvesting. It also has 14 million animals, including cattle, pigs, and poultry, all producing manure waste daily (Government of Saskatchewan, 2008). As much of Saskatchewan's population is rural, there are great opportunities to decentralize energy sources and provide farmers or small communities with the ability to self-sufficiently produce fuels from processing common wastes found on their own farms. This can be achieved through the pyrolysis of a variety of agricultural residues. From the literature, it was found that, besides the feedstock, temperature is the most important variable during the process; although particle size, moisture content, ash content, residence times, and many other operating conditions can impact the formation of products as well.

Biomass has received a lot of attention over the past couple decades, as the emerging bioenergy industry has been promoted as a means of simultaneously improving energy security, improving rural economies, and helping to mitigate the threat of global climate change. Concerns have been raised, however, that the bioenergy industry will exacerbate problems of global energy security because of competition between bioenergy production and food production for land and other resources. Examples that have propelled these concerns are the industries that have commercialized the production of so-called first generation bio-fuels from biomass: bio-ethanol (from starch and sugar products such as wheat) and bio-diesel (from oil crops like rapeseed and sunflower) (Forson et al., 2004).

Thus, there is a demand for alternative, non-edible biomass resources in the bioenergy sector. Options include forest and agricultural residues such as sawdust, straws, and manure. Possible conversion technologies of said biomass are as follows:

- *Fermentation processes* (conversion of the cellulosic materials to low molecular weight sugars through chemical and/or physical processes; then, subsequent conversion to ethanol via fermentation).

- *Gasification* to produce bio-syngas for further upgrading to methanol or gas/diesel.
- *Liquefaction* (conversion of biomass to liquid fuel) with further upgrading either through gasification or through deoxygenation, hydrogenation, etc., to produce gas/diesel range hydrocarbons and value added chemicals.

The primary liquefaction process of interest is the pyrolysis of biomass. Pyrolysis (or devolatilization) is the thermal decomposition of materials in the absence of oxygen. This thermochemical process can be used to transform unstable biomass (~17MJ/kg) and other organic materials into a more stable, high-energy-density liquid known as bio-oil (~22MJ/kg), a high-energy-density solid known as biochar (~18MJ/kg), and a relatively low-energy-density gas known as syngas (~6MJ/kg) (Laird et al., 2009).

Pyrolysis is a thermal technology that decomposes organic materials by heat (300-600°C) in the absence of oxygen. A carbonaceous (biomass) particle is heated and volatiles are released, producing a char product, and a liquid oil and gas from the condensable and non-condensable volatiles. The process is dependent on the properties of the biomass and determined the structure and composition of the products.

1.2 Pyrolysis

Conventional or "slow" pyrolysis has been used for thousands of years to produce charcoal (Mohan et al., 2006). The feedstock can be held at temperature or slowly heated, and the vapour residence time is typically 5 to 30 minutes. "Fast" pyrolysis uses much faster heating rates. There are four essential features of a fast pyrolysis process: very high heating and heat transfer rates; carefully controlled pyrolysis reaction temperature, often 400 to 500°C, although up to 800°C has been observed (Demirbas, 2009); a short vapour residence time (less than 2 seconds typically); and rapid cooling of pyrolysis vapours and aerosols to give bio-oil. The general changes that occur during pyrolysis are described below (Mohan et al., 2006):

- Heat transfer from a heat source increases temperature inside the fuel.
- The initiation of primary pyrolysis reactions at this higher temperature releases volatiles and forms char.
- The flow of hot volatiles toward cooler solids results in a heat transfer between hot volatiles and cooler unpyrolyzed fuel.

- Condensation of some of the volatiles in the cooler parts of the fuel, followed by secondary reactions, can produce tar.
- Autocatalytic secondary pyrolysis reactions proceed while primary pyrolytic reactions simultaneously occur in competition.
- Further thermal decomposition, reforming, water gas shift reactions, radicals recombination, and dehydrations can also occur, which are a function of the process's residence time/temperature/pressure profile.

Fundamental research over the last two decades on fast pyrolysis has shown that high yields of primary, non-equilibrium liquids and gases, including valuable chemicals, can be obtained from biomass feedstocks. However, as the chemical composition of biomass differs from that of fossil feeds (such coal, oil shales), the pyrolytic chemistry also differs. The time frame for pyrolysis with the goal of producing oils rather than char, termed fast pyrolysis, is much faster where heating occurs in 1 to 10 seconds. Liquid yields from pyrolysis should be in the range of 40 to 55 wt% with a heating value of approximately 20 to 22 MJ/kg, a pH of 2 to 4, and a composition including many oxygenated constituents along with some hydrocarbons. This is why drying and an operating temperature of 400 to 500°C are recommended. Biochar yields can be anywhere in the range of 15 to 40% on a weight basis of the biomass feedstock (Brown et al., 2010). The remainder is gas product.

1.2.1 Technology

Design variables required for fast pyrolysis include: feed drying, particle size, pretreatment, reactor configuration, heat supply, heat transfer, heating rates, reaction temperature, vapour residence time, secondary cracking, char separation, ash separation, and liquid collection.

Several pyrolysis designs have been studied in the literature including: fluidized bed, ablative screw reactor, rotary cone, centrifuge reactor, auger, and vortex (cyclonic) reactors (DOE, 2005). New technologies have expanded to mobile pyrolysis technologies. A variety of skid-mounted (i.e., mobile) pyrolysis systems are being developed, including the auger type reactor by ABRI Tech.

ABRI Tech Inc. (Ottawa, ON) has been a pioneer of mobile pyrolysis technology. The company's multiple 1 tonne/day pyrolysis units are being utilized across Canada and within the United States. Natural Resources Canada (NRCan) has been involved in the assessment

of pyrolysis oil as a feedstock for combusting in boilers, and is presently arranging the utilization of auger type ABRI technology for production of pyrolysis oils in their laboratories.

Auger technology is adapted from a Lurgi process for coal gasification. Hot sand and biomass particles are fed at one end of a screw. The screw mixes the sand and biomass and conveys them along. There are several advantages with an auger-type reactor: it is compact and does not require carrier gas; it operates at lower process temperatures (Mohan et al., 2006); and it operates as a continuous process with good control of the biomass residence time. However, sand must be reheated in a separate vessel, and mechanical reliability is a concern. Large-scale commercial implementation is only recently occurring.

Augers are used to move biomass feedstock (such as agricultural residues, forestry residues) through an oxygen-free cylindrical heated tube. A passage through the tube raises the feedstock to the desired pyrolysis temperature (which can be in the range of 400 to 800°C), causing it to devolatilize and gasify. Char is produced and gases are condensed as bio-oil and non-condensables are collected as biogas. The design consequently reduces the energy costs relative to some other designs.

The fast pyrolysis of agricultural residues in a portable auger reactor has the potential to contribute to Saskatchewan's rural energy needs. However, the feed complexity and variety makes it difficult to define standard processes. Feedstock drying to 10% moisture or less is an important part of the pyrolysis process, as the feed moisture directly affects the products.

The recommended processing procedure for pyrolyzing biomass is:

- Biomass size reduction – grinding or milling
- Biomass drying to >10% moisture content – air or oven drying
- Heat biomass before reaching "pyrolysis zone" – 110 to 150°C
- Pyrolysis in auger reactor – 400 to 500°C, short residence time of 1 to 10 s

The development of portable pyrolysis technology is desirable, as it can be used for evaluation of various feedstocks from different sources or industries, particularly at remote locations, or of feedstocks whose presence in a central urban location may be undesirable due to existing regulations or public nuisances such as smell.

1.2.2 Feedstock Composition: Expected Chemicals from the Pyrolysis of Biomass Feedstocks

Several studies reported that some pyrolysis properties such as feedstock chemical composition, particle size and moisture content, pyrolysis temperature, and heating rate significantly affect bio-oil yield and properties (Demirbas, 1998; Bonelli et al., 2001; Deboudi et al., Boateng et al., 2006; Onay, 2007; He et al., 2009). Furthermore, according to Huber et al (2006) the exact composition of the bio-oil is dependent on the feedstock composition (including contaminants like dirt and moisture content) and pyrolysis conditions, organic nitrogen or protein content of the feedstock, heat transfer rate, final char temperature during pyrolysis, time and temperature of vapours in the reaction, efficiency of the char removal system, and efficiency of the condensation equipment to recover the volatile components from the non-condensable gas stream.

Because of the original biomass's complexity, the composition of the bio-oil product is slightly unpredictable and contains a plethora of constituents. Huber et al (2006) reported bio-oil from any source to contain acids (including acetic and propanoic), alcohols (methanol, ethylene glycol, ethanol), ketones (acetone), aldehydes (acetaldehyde, formaldehyde, ethanedial), miscellaneous oxygenates (glycolaldehyde, acetol), sugars (1,6-anhydroglucose, acetol), furans (furfural, furfural), phenols (phenol, methyl phenol, dimethyl phenol), and guaiacols (isoeugenol, eugenol, 4-methyl propyl syringol).

The multicomponent bio-oils mixtures are derived primarily from depolymerization and fragmentation reactions of the three building blocks of lignocellulose: cellulose, hemicellulose, and lignin. Naik et al. (2009) summarized the cellulose, hemicellulose, and lignin contents of a variety of Canadian biomass. This can be seen below in **Table 1.1**.

1.1: Cellulose, Hemicellulose, and Lignin Content of Various Canadian Biomass Samples as Determined through Acid Treatment and Subsequent HPLC

Biomass	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)
Wheat straw	34.6 ± 0.2	29.3 ± 0.3	21.3 ± 0.3
Barley straw	32.5 ± 0.4	25.7 ± 0.2	23.0 ± 0.5
Flax straw	28.7 ± 0.2	26.8 ± 0.2	22.5 ± 0.4
Timothy grass	31.5 ± 0.2	27.5 ± 0.3	24.0 ± 0.6
Pinewood	39.0 ± 0.3	34.0 ± 0.3	12.0 ± 0.5

1.2.3 Temperature

Temperature is the pyrolysis process parameter with the most significant effect on products. This is especially true in an auger-style reactor where pressure is not used.

A temperature of 450°C was found by Ingram et al. (2008) to be optimal and produced liquid yields of 40 to 55 wt% depending on the wood feedstock used.

Putun et al. (2005) studied the effect of temperature on the pyrolysis of cotton stalk. They found that as temperature increased, solid formation decreased while liquid and gas formation increased. **Table 1.2** below shows the effect of process temperature reported by Putun et al. (2005) on product yields; these findings were confirmed by Aguiar et al.'s (2008) study with orange peel and Lee et al. (2005) with rice straw.

1.2: Effect of Temperature on the Yields of Pyrolysis Products from Cotton Stalk Particle Size (1.2 mm, heating rate: 7°C/min) (Putun et al., 2005)

Product yields (wt%)	Temperature (°C)			
	400	450	500	700
Solids	30.30	29.17	27.93	25.56
Liquids	20.28	22.38	23.02	18.59
Gas	26.59	26.51	27.02	32.02

From the literature listed, it is evident that the chemistry of bio-oils can be manipulated by changing the thermal conditions. Increasing the temperature (cracking severity) lowers the molecular weight distribution in the resulting oils and produces more gas. At very high temperatures, dehydrogenation/aromatization reactions become favourable, which eventually lead to larger polynuclear aromatic hydrocarbons (PAHs) and, eventually, increases in carbonization. Elliot (1986) described the relationship between the types of compounds in the products and the temperature to which the vapours were exposed before quenching. He stated that at 400°C, mixed oxygenates were favoured, at 500°C phenolic esters, at 600°C alkyl phenolics, at 700°C heterocyclic ethers, and at 800°C polycyclic PAHs. As the temperatures increased, alkyl groups cleave from aromatic compounds. Eventually, the aromatic compounds condense into polycyclic aromatic hydrocarbons, which lead to polymerization and carbonization. Therefore, it can be seen that for liquid and char optimization, lower temperatures of 400 to 500°C are favoured. However, if gas formation is to be optimized, higher temperatures of 600 to 800°C are preferred.

1.2.4 Moisture Content

The effect of moisture content can be viewed from two perspectives. White and Plaskett (1981) reported that excess oxygen and water present in biomass was helpful in converting biomass carbon into gaseous fuels. Moisture within the biomass encourages gas formation. Furthermore, during gasification, moisture content as high as 65 wt% was tolerable. The water content, higher hydrogen/carbon ratio, and low sulphur content make gasification of biomass preferable to gasification of coal. However, the same benefit of moisture content is not seen during pyrolysis.

He et al. (2009) studied the effect of biomass (switchgrass) moisture content and temperature on the pyrolysis process. Results showed that the main effects of the two factors, as well as the interaction of the two factors, significantly affect the product yields, all the physical properties, and the majority of the measured chemical properties.

Therefore, the physical adjustment of the bio-oil properties needs to be prioritized, as not all can be optimized simultaneously.

1.3 Pyrolysis Feedstocks

A wide variety of biomass feedstocks have been used in pyrolysis. The available biomass of the world is 220 billion metric tonnes per year, or 4500EJ (10^{18} J) (Naik et al., 2009). These include agricultural residues such as sugar cane bagasse, straw, and hulls;; urban waste such as waste tires (Tang et al., 2003); and woods and wood products, either hardwoods such as oak, birch, elm, maple, and ash, or softwoods such as willow, spruce, fir, and pine.

Plant biomass is primarily made up of carbohydrate polymers and oligomers (mainly cellulose and hemicellulose), lignin, and organic extractives and inorganic minerals (4–10%) (Mohan et al., 2006). Cellulose is a high molecular weight polymer of glucopyranose (a simple sugar), and cellulose fibres provide strength and comprise 40 to 50% of dry wood biomass. Cellulose degradation occurs at 240 to 350°C. Hemicellulose is a lower molecular weight mixture of monosaccharides (simple sugars) such as glucose, mannose, galactose, xylose, and arabinose. Hemicellulose decomposes at 200 to 260°C giving rise to more volatiles, less tars, and less char than cellulose. Much of the acetic acid liberated during pyrolysis is attributed to hemicellulose (Mohan et al., 2006). Lignin is an amorphous cross-linked resin with no exact structure. Lignin decomposes when heated to 380 to 500°C. Lignin yields phenols, and more residual char than cellulose.

Saskatchewan produces many agricultural residues that could serve as feedstock for pyrolysis such as straws from grain and seed crops, hulls and husks, and livestock manures. Canada is the fourth largest producer of wheat in the world (Naik et al., 2009) and produced 34% of the world's flax, yielding 633,500 metric tonnes in 2007 (Laux, 2009). Each feedstock differs, however, with different considerations for use in pyrolysis. Some biomass feedstocks common to the Saskatchewan prairies are discussed in more detail below.

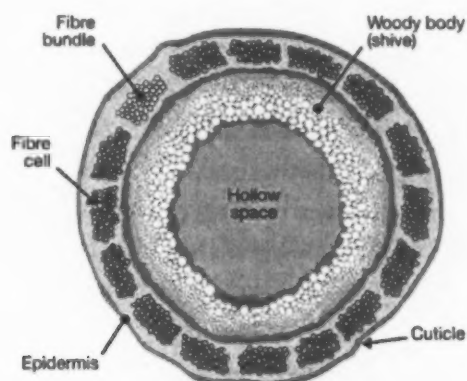
1.3.1 Wheat Straw

When wheat grain is harvested, it leaves behind straw, as much as 37.3 million tonnes annually in Canada (AAFC, 2009). Straw is defined as the dry stalks of cereal plants, left behind after the grain and chaff have been removed. Chaff is defined as the dry, scaly protective casings or husks of the seeds of cereal grain. Waste straw should contain no chaff, as the seeds have been removed. Furthermore, the chaff may be separated from the plant by winnowing or threshing. Chaff and straw are inedible for humans, but are commonly used as livestock fodder, tilled back into the soil as soil amendment (erosion control, fertilizer, soil quality and tilth, and soil moisture conservation), or as a waste material ploughed into the soil or burnt. Canada Produces 15 million metric tonnes of cereal straw each year which could conceivably be removed for biomass energy (Sokhnsanj et al., 2006) even after deductions for soil conservation and livestock feed.

1.3.2 Flax Straw

With the harvesting of flaxseed each year, 720,000 metric tonnes of flax straw are produced as well; of which 570,000 tonnes could be sustainably removed (Wood and Layzell, 2008). Unlike wheat, the tough stem fibres in flax straw decay slowly over time, making it difficult to incorporate the straw into the soil after harvest (Flax Council of Canada, 2002). Traditionally, the method of dealing with flax straw was to burn it directly on the field (Flax Council of Canada, 2002), a practice which is now banned in some areas. The two major fractions of flax straw are shive and fibre. Shive is also known as core flax fibre and comes from the inside of the flax stem. It is responsible for holding the plant rigid during growth and is commonly referred to as the "woody part" of flax (Sain and Fortierb, 2002). The fraction is described as soft, lustrous, and flexible (Flax Council of Canada, 2002). It is stronger than cotton fibre, but less elastic. **Fig. 1.1** below depicts the location of flax fibre and shive through a cross-sectional view of the flax stem. Flax is typically "retted" (degradation of pectins which bind fibres to straw with exposure to rain and sun) prior to use, particularly if the fibre fraction will require separation to be used in other products. Retting is also a natural result of storage of flax straw

outdoors. Retted flax will separate significantly into the two fractions during simple grinding processes, even without special attention to separation. The fibrous fraction of flax straw can be difficult to process due to its soft flexible nature. Flax straw frequently clogs tillage equipment.



1.1: Cross section of a flax stem (NRC Canada, 2009).

The compositions of flax straw, fibre and shive differ significantly. Naik et al. (2009) quantified the cellulose, hemicellulose, and lignin contents in flax straw through acid hydrolysis and subsequent chromatography. Li (2008) carried out an analysis on the chemical composition of flax fibre, and the results are shown in **Table 1.3**. As the shive content increased, lignin content also increased. Flax shive contained more lignin and hemicellulose, and less cellulose, than pure flax fibre. From this data, it can be concluded that the shive contains the most lignin, whereas the fibre contains the most cellulose.

1.3: Chemical Composition of Flax Fibers (Li, 2008)

Materials (purity of fibre)	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Fibre I (98-99%)	83.77	5.79	1.16
Fibre II (85%)	79.99	6.76	2.38
Flax shive	47.22	11.52	20.89

Uses for Flax Fibre and Shive

Because flax fibres are easily separated from retted straw when submitted to large scale grinding processes, the fibre can be removed from the pyrolysis process and set aside for use in other products and processes. Flax fibre is commonly used in linen, twine and rope

production (Wardley, 1967). Extracted flax fibre can be used for production of specialty papers, such as paper for cigarettes, currency, teabags, and artwork. Furthermore, flax fibre can be used to strengthen recycled paper (Flax Council of Canada, 2002).

In recent years, a flax straw processing plant was set up in Canora, Saskatchewan. In addition to extracting flax fibre for use in specialty paper production, this plant produces fibres to replace the fiberglass fibres presently being used in plastic composition to make automotive parts like dashboards, decking, sewer pipes, and septic tanks. Many everyday plastic products contain fiberglass to give strength, reduce weight and/or reduce cost. In addition, flax fibres take less energy to manufacture and are easier to decompose or burn than traditional fiberglass. The demand for flax fibres in plastic composites has grown by more than 50% in Europe in recent years and this trend is now appearing in North America. This demand stems from automotive dealers who are under pressure to make their vehicles lighter and cheaper while using more environmentally friendly materials (Flax Council of Canada, 2002).

To date, flax shives have not found many high-value end uses. In Europe and Asia, flax shives are often used to make particleboard, but wood particles are so inexpensive in North America that this is not a viable commercial use at this time. Flax shives are therefore often burnt as fuel or used as horticulture mulch, or simply burnt on farm site as a waste management technique.

1.3.3 Poultry Litter

Poultry litter is an interesting feedstock for pyrolysis, as the safe and economical disposal of poultry litter is a continuing problem in the poultry industry. Over 25 million birds are produced annually in Saskatchewan alone (Saskatchewan Ministry of Agriculture, 2009). Current disposal methods such as land application and feeding to cattle are now under pressure because of pollution of water resources due to leaching and runoffs, and because of concern for disease contamination of the food chain. Pyrolysis could provide an alternative stream for poultry waste and it destroys any microorganism in the process. Poultry litter behaves much like agroforestry residues during the pyrolysis reaction, as it is typically composed of either wood chips or straw bedding in combination with the chicken manure, along with spilled feed, feathers, and dirt (Singh et al., 2007).

Effect of Ash Content

Both the feed and the pyrolysis products of poultry litter were extensively characterized by Agblevor et al. (2010). It was concluded that poultry litter contained relatively large fractions of ash, which are rich in potassium, phosphorus, calcium, and magnesium. The composition and properties of the bio-oil depend on the poultry litter source and show a considerable variation among samples, with increased nitrogen content being consistently observed. The ash content of the biochar reported by Agblevor et al. (2010) ranged from 24 to 54 wt% and was very rich in inorganic components such as potassium and phosphorous. This shows evidence that the ash content of the sample is directly related to char formation.

Das et al (2008) studied the pyrolysis of pine chips and poultry litter in an auger reactor. They also reported that poultry litter yielded more char and less liquid than wood chips. They attributed this to the larger content of proteins and ash present in the poultry litter.

1.3.4 Feedstock Processing and Storage

Since biomass varies widely in composition and is often only available seasonally, logistics and storage are two of the major challenges for consistent operations. Biomass composition varies not only with species, but also with location, time, and climate. In order to operate a pyrolysis unit throughout the year and maintain the desired product quality, an uninterrupted supply of uniform biomass is necessary. Depending on the biomass type, conventional methods of transportation and storage can become expensive and unfeasible. Storage capabilities are needed to accommodate the logistics of biomass conversion operations. This requirement arises primarily from supply and demand imbalances due to small scale operation and limited manpower, energy prices, growing seasons, and weather conditions. Storage of woody biomass harvested during excess production and delivery when demand exceeds supply are important steps to ensure a reliable, continuous supply of feedstock. Pre-processing and proper storage on the upstream side are equally important in a biomass utilization facility. Various methods of particle size reduction such as chipping, grinding, shredding and bundling, along with different ways of drying, protect biomass from degradation. Pelletization of biomass material can positively impact the ease of transportation and handling.

1.3.4.1 Effect of Particle Size on Pyrolysis Products

Depending on the natural state of pyrolysis feedstocks, size reduction prior to pyrolysis is required. The main reason for this reduction is easier drying before pyrolysis and heat transfer during pyrolysis.

Aguiar et al. (2008) studied the effects of temperature and particle size of orange peel residue in a fixed bed pyrolysis reactor and concluded that temperature plays a much more significant role in product formation than particle size.

Sensoz et al. (2000) conducted rapeseed experiments in a fixed-bed reactor at 500°C. Pyrolysis oil and char yields from rapeseed were found to be dependent on particle size, with oil yield showing a maximum with the largest particle size (0.85–1.8 mm).

Scott et al. (2009) found that, at their particular residence time, the coarsest particles were least affected by temperature variation and the finest were most affected. It can be postulated that this phenomenon was due to the larger particles not heating up as rapidly and the smallest particles either overheating or blowing from the reactor too quickly, as is suggested by the higher char yields associated with the smaller particles. The highest liquid yields were obtained with the moderate sized particle of 105 to 250 µm. This is important to consider when fine dust is created during a grinding process.

Putun et al. (2005) studied pyrolysis of cotton stalks in a fixed-bed reactor at atmospheric pressure and 550°C. In this study, bio-oil yields remained unchanged for the particle size range studied (0.25–1.8 mm). Therefore, it appears that particle size has little effect on liquid yield. However, based on various studies, it would appear that narrow ranges of particle sizes are desirable, particularly for consistent results. The ranges of particle sizes that are frequently used in pyrolysis are summarized in Table 1.4.

1.4: Common Particle Sizes Used in Literature Where the Effects Were Not Studied

Reference	Material	Particle size (mm)
Hassan et al., 2009	Pine/cottonwood	1–3 mm
Ingram et al., 2008	Pine wood/oak bark	2–4 mm
Tushaw et al., 2010	Flax straw	1 mm
Wang et al., 2010	Wheat straw	0.05–0.2 mm

1.3.4.2 Biomass Drying

Fast pyrolysis requires a feedstock of less than 10% moisture content, but there is often an optimization to be carried out between moisture content and conversion efficiency. The actual moisture content required for the conversion process will therefore vary somewhat

between conversion facilities. As fast pyrolysis is usually used to maximize oil production, this is undesirable.

Biomass as received can have a moisture content in the range of 50 to 60% (wet basis), depending on the feedstock (Mitchell et al., 1989). However, some agricultural residues are much more appealing, as they have lower initial moisture content and have been partially processed in harvesting or collection. Straws from wheat, barley and flax are examples of lower-moisture-content feedstocks in the range of 10 to 20% (Tushaw et al., 2010). Furthermore, straw is generally chopped, baled and partly dried during harvest of the grain. This makes agricultural grain residues cheaper to pre-process prior to pyrolysis and, therefore, desirable. For forestry wastes and vegetable-derived matter with typically high moisture contents (50–60%), passive drying (air drying) and active silo drying during summer can reduce the moisture to 12 to 30% (Gustafsson, 1988).

1.4 Pyrolysis Products

The major desirable product of fast pyrolysis processes of biomass is oil. Pyrolysis oils are generally dark (brown, black, or green) organic liquids comprised of highly oxygenated compounds. Although this product is termed as an oil, it is more similar to tar in properties and appearance (Dermibas, 2009). Pyrolysis oil is made up of the condensable components of biomass volatilized during pyrolysis. The heating value ranges from 15 to 22 MJ/kg. The lower heating value of bio-oils relative to mineral oils is due primarily to the oxygen content of the former (Oasmaa and Meier, 2005). Pyrolysis oils typically have 20% water content [with up to 50% being observed (Mohan et al., 2006)] and are acidic with a pH of 1.5 to 3.8. The density range is 1.2 to 1.3 kg/L, which is significantly higher than diesel. The viscosity can range from 20 to 850 mPa·s (at 40°C). Normally the viscosity increases with water content of the oil. Bio-oil cannot be dissolved in water, but is miscible with polar solvents such as methanol. Pyrolysis oil typically has a pour point of -12 to -33°C, and a flash point of 40 to 100°C. The oxygen content is 40 to 50%, mostly from bound "water" content, and is sulphur free. The carbon residue is 17 to 23 wt% (0.13% ash). The cetane number of pyrolysis oil is only 10 (Martelli, 2010). While the exact composition of bio-oil depends on the biomass source and processing conditions, a typical composition is as follows: water 20 to 28 %; suspended solids and pyrolytic lignin 22 to 36 %; hydroxyacetaldehyde 8 to 12%; levoglucosan 3 to 8 %; acetic acid 4 to 8 %; acetol 3 to 6 %; cellubiosan 1 to 2 %; glyoxal 1 to 2 %; formaldehyde 3 to 4 %; formic Acid 3 to 6%. (Dynamotive, 2011).

Pyrolysis oils contain compounds which, during storage and handling, can react with themselves to form larger molecules (Oasmaa and Czernik, 1999). Rapid quenching of volatiles and aerosols into the liquid oil results in the presence of many reactive intermediate products of biomass degradation. These contribute to its unusual attributes. The viscosity increases to a maximum over a period of 12 months due to this polymerization, as well as etherification and esterification, and the oil is not stable under conditions of air exposure and degassing. The aging rate depends on the chemical composition, and therefore on the feedstock, the process conditions, and the efficiency of solids removal and product collection (Oasmaa and Czernik, 1999). For example, the viscosity of a hardwood pyrolysis oil was reported to double after one year of storage at room temperature, after one week at 60°C, and 1 day at 80°C. The gain rate can be reduced by simple fuel additives (Dermibas, 2009) such as methanol and water.

Char is a solid product made up of the residues of incomplete organic pyrolysis of biomass. What is termed "charcoal" is a char product, made from wood rather than other biomass sources. Pyrolysis gas is made up of carbon dioxide, carbon monoxide, hydrogen, methane and other hydrocarbons, and nitrogen. The distribution of pyrolysis products depends on feedstock composition, heating rate, temperature, and pressure (Kovacs, 2001).

1.4.1 Optimized Conditions for Pyrolysis

Dermibas (2009) predicted that if wood was completely pyrolyzed, the resulting products would be what should be expected from pyrolyzing the three major components (cellulose, hemicelluloses, and lignin) separately, and he conducted his literature review on that basis. Therefore the devolatilization behaviour of biomass should be related to that of those three chemical constituents. For biomass, the devolatilization behaviour is predictable. The weight loss at temperatures less than 100°C was for loss of high volatiles, 100 to 130°C for loss of water, 130 to 250°C for volatile compounds, 250 to 350°C for hemicellulose, 350 to 500°C for cellulose, and greater than 500°C for lignin. With fast pyrolysis, the temperature increases very quickly (less than 2 s) and volatilization occurs almost instantaneously.

Through examination of the degradation of each separate component, he concluded that for maximization of the yield of liquid products resulting from biomass pyrolysis, a process with lower temperature, high heating rate, and short gas residence time would be required. For a high char production, a low-temperature, low-heating-rate process would be chosen. For

maximization of the yield of fuel gas resulting from pyrolysis, a high temperature, low heating rate, and long gas residence times would be preferred.

However, there is currently no clear literature on optimized conditions for particular feedstocks in an auger reactor system. The studies currently published in the literature are scattered over different biomass types and different combinations of pyrolysis parameters, paying little attention to improving bio-oil properties via adjustment of pyrolysis condition. Furthermore, He et al. (2009) concluded that there is no single, clear-cut optimal condition that can satisfy the criteria for a bio-oil product with all the desired properties. Trade-offs should be balanced according to the usage of the end-products, given the heterogeneous nature of biomass feedstocks and the complex reactions occurring during fast pyrolysis. He et al. (2009) recommended that catalysts be introduced into future pyrolysis research in order to increase the selectivities to desired products and to establish norms and standards for bio-oil production according to the usages of pyrolysis products. However, based on the current literature we can infer general statements about the effect of each process parameter examined above:

- Through the examination of decomposition of each chemical component it can be concluded that biomass with a high lignin fraction (agricultural residues) will yield less liquid and more char.
- Liquid yield can be optimized though moderate temperature of 350 to 450°C. It was observed that as temperature was increased, liquid products decreased.
- Char content increases as moisture content increases. Moderate moisture conditions and low temperature are preferred for high yield of bio-oil.
- pH of bio-oil can be slightly increased from 2.7 to 3.3 by increasing the process temperature to 550°C
- The heating value of bio-oil could be increased from 16.6 MJ/kg to 19.6MJ/kg by decreasing the process temperature to 450°C
- A decrease of water content in the bio-oil from 31.6 to 20.1 wt% was observed at a process temperature of 450°C and low feedstock moisture content of 5 wt%.
- Low ash content is desired for liquid formation, as high ash content leads to char formation.

1.5 Product End-Uses

1.5.1 Oil

Bio-oil can serve as a feedstock for production of fuels and chemicals. Bio-oils can be used as combustion fuels and for power generation, for production of chemicals and resins, when upgraded as transportation fuel to replace fossil fuels, for production of anhydro-sugars like levoglucosan, as binders for pelletizing and briquetting of combustible organic waste materials, as a wood preservative, and in making adhesives. Comparison between wood pyrolysis oil and heavy heating oil can be seen below in **Table 1.5**.

1.5: Typical Properties of Wood Pyrolysis Bio-oil and of Heavy Fuel Oil (Oasmaa and Czernik, 1999)

Physical Property	Bio-oil	Heavy Fuel Oil
Moisture content (wt%)	15–30	0.1
pH	2.5	–
Specific gravity	1.2	0.94
Elemental composition (wt%)		
C	54–58	85
H	5.5–7.0	11
O	35–40	1
N	0–0.2	0.3
Ash	0–0.2	0.1
Heating Value (MJ/kg)	16–19	40
Viscosity (at 50 C) mPa·s	40–100	180
Solids (wt%)	0.2–1	1

Combustion tests performed using a variety of burners and internal combustion engines have demonstrated that bio-oil has potential to be used as a fuel oil substitute (Oasmaa and Czernik, 1999). Although bio-oil is not suitable as a transportation fuel, it can be upgraded to a transportation fuel. One option is to gasify the bio-oil and convert the resulting syngas to synthetic gasoline or diesel through Fischer-Tropsch catalytic synthesis (Laird et al., 2009). Another approach is to hydrocrack bio-oil to transportation fuels in a manner similar to the refining of petroleum to gasoline. This process is economically attractive, as it could employ the infrastructure at existing refineries (Laird et al., 2009). Bio-oil can be burned in industrial boilers; however, its use as an industrial fuel typically requires the boiler be equipped with

stainless steel or plastic-lined, fuel-injection components and storage tanks to resist corrosion, a system that heats and/or stirs the bio-oil during storage to prevent gelling, and a system that pre-heats the incoming bio-oil to the flash point before nebulisation to improve burn efficiency (Laird et al., 2009).

Emulsions of bio-oil and diesel oil have been successfully created using emulsifiers (Oasmaa and Czernik, 1999; Qi et al., 2008). Bio-oil can be converted to gasoline with reasonable hydrogen consumption using mild hydrotreating followed by hydrocracking (DOE, 2006). Bio-oils can also be used, because of their reactivity, in thermosetting resins and other wood-bonding methods (Johnson and Chum, 1986). Bio-oils can also be gasified to produce syngas.

Given the large range of chemicals present in bio-oils, it may be economically attractive to first recover valuable bio-chemicals from the bio-oil for pharmaceuticals and food additives. The remainder of the bio-oil can then be combusted to generate electricity or converted to syngas from which chemicals and fuels can be synthesized.

One major obstacle to commercial applications of bio-oils is the variability of properties and lack of standard quality specifications for these oils required by the end-users (Oasmaa and Czernik, 1999).

1.5.2 Char

Biochar can be used as solid fuel in boilers, either as converted briquettes alone or mixed with biomass; used in production of activated carbon and in carbon-nano-tubes; or in further gasification to obtain hydrogen-rich gas by thermal cracking. Biochar is a combustible solid (~18 MJ/kg) that can be burned to generate heat energy in most systems that are currently burning pulverized coal. If the char were to be burned as a coal substitution, knowing its heating value is crucial. Furthermore, there are new emerging uses of biochar. Biochar is a carbon-rich material that is capable of resisting chemical and microbial breakdown, allowing it to be used to sequester carbon for extensive periods of time. In addition to sequestering carbon, field studies have shown that biochar works in conjunction with compost and fertilizers to improve crop productivity (Brown et al., 2010) and the value of biochar as a soil amendment is reported (Bruun et al., 2011; Brown et al., 2010), including a project in collaboration with SRC presently funded by the Agriculture Development Fund. Other work is underway to examine the value of char for removing odorants from air streams, and

organic and inorganic contaminants from waste-water streams. Biochar can also be used as a feedstock for activated carbon. Furthermore, if the char was to be used as a soil amendment or catalyst, the acidity and textural properties would become significant.

1.5.3 Gas

Pyrolysis gas (also termed off-gas and syngas) containing significant amounts of carbon dioxide along with methane can be used as a fuel for industrial combustion purposes. It can also be upgraded to fuels. Ratcliff et al. (2002) successfully demonstrated the operation of a spark ignition engine on wood-derived pyrolysis gas.

2. METHODS AND MATERIALS

2.1 Equipment – Portable Pyrolysis Unit

A 1-tonne per day pyrolysis unit was acquired from ABRI Tech Inc. (Ottawa, ON, Canada), designed to be operated in a portable fashion. This unit was mounted on a trailer to make it portable and modified to meet the requirements of operation at our facility. The process flow diagram for the portable pyrolysis unit is provided in Figure 2.1. It primarily consists of three skids – the drying skid, hydraulic skid and pyrolysis skid – which are installed on a trailer for portability. In addition, some auxiliary equipment must be included, such as an air compressor, a burner, a propane tank, and barrels. Inputs to the unit include biomass feed stock, electricity and propane; and products from the unit are gas (off-gas or syngas), liquid bio-oil and solid bio-char.

As shown in Figure 2.1, wet biomass is fed to the dryer first to remove most of the water. Heat required for the dryer comes from the combustion of produced off-gas from the pyrolyzer and/or propane depending on present operation. There are two output streams from the dryer: the stack gas and the dried biomass, the latter having moisture content desired at typically lower than 10%. In the current design, dried biomass is first collected in a barrel, and then manually fed to the pyrolysis reactor.

The pyrolysis skid includes a reactor for pyrolysis, a char recovery system, a condenser and a bio-oil tank. Primarily using propane as the heating source for pyrolysis reactions, there are four output streams from the pyrolysis skid: liquid bio-oil (~60 wt%), solid bio-char (~20 wt%) off-gas (~20 wt%), and the stack gas stream coming from the combustion of propane.

The pyrolysis reactor is an auger reactor. The stainless wall of the auger is also used as the surface for heat transfer; therefore, the reactor itself is also a heat exchanger. To improve the heat transfer efficiency, a solid-form heat carrier (steel shot and currently ceramic shot) is forced to circulate within the system.

The hydraulic skid includes a hydraulic pump, a bio-oil circulating pump, a glycol circulating pump, a radiator, and a control and monitoring system. The hydraulic pump is used to provide driving force for four augers and one rotary valve through circulation of hydraulic oil. The bio-oil circulating pump is used to circulate and discharge bio-oil; low temperature bio-oil is also used to condense newly produced bio-oil vapour. The glycol circulating pump

and the radiator are used as a cooling system to cool down produced bio-oil. The unit also requires electrical power.

Fig. 2.1 provides estimated mass and energy balance information based on the manufacturer's estimate for pyrolysis of wood chips.

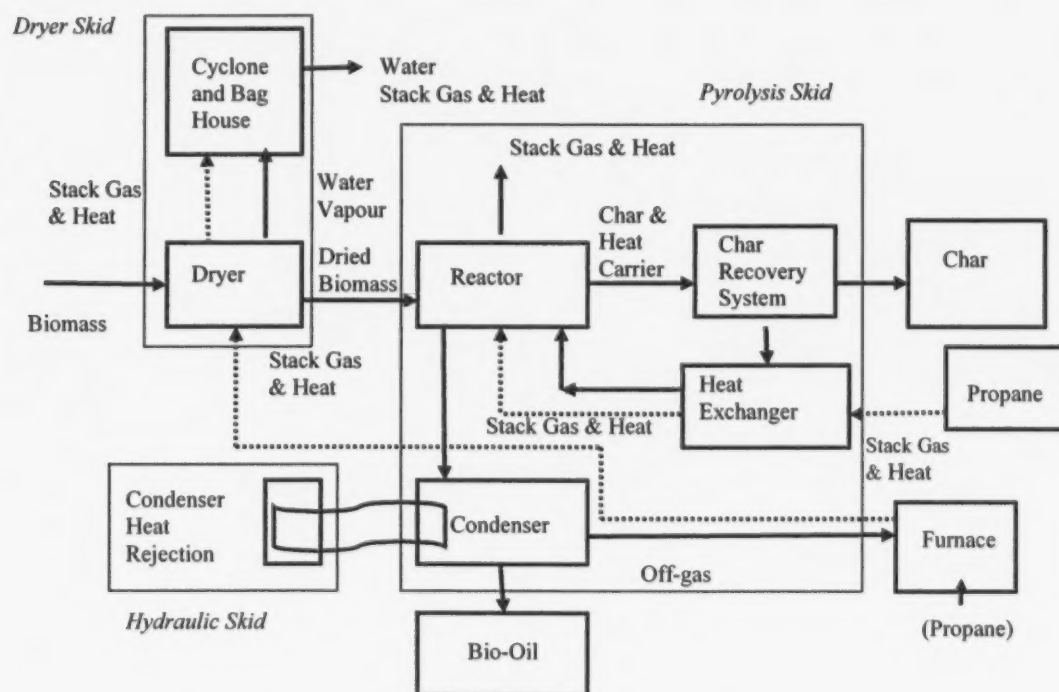


Fig. 2.1: Process flow diagram of the portable pyrolysis unit.

A photograph of the pyrolysis unit is included as **Fig. 2.2**. Detailed schematics and photographs of the unit in operation are provided in the Appendices.

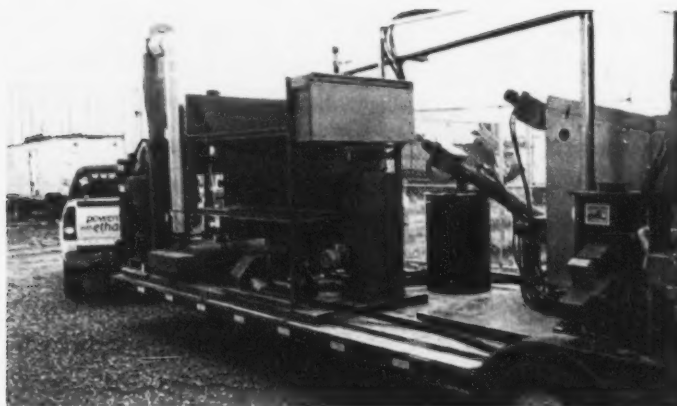


Fig. 2.2: Transporting the pyrolysis unit.

2.2 Feedstocks

Baled wheat straw (AC Lillian) was obtained from filler plots on the Agriculture and Agri-Food (AAFC) South Farm, Swift Current, SK, in October 2010. Flax straw was baled at the Simonson Farm located near Neidpath, SK. The variety was Sorrel. Additional retted flax came from Brandon, MB, from the Manitoba Zero Till Research Farm. The flax (Prairie Blue) was grown and baled in the fall of 2009. Sorted flax shives were purchased from SWM Intl., (Winkler, MB). The poultry litter was obtained from Advanced Poultry Technologies (Saskatoon, SK). Wheat straw and retted flax straw were reduced using a tub grinder at the University of Saskatchewan dairy farm. The mixed hardwood sawdust was obtained from Hy-Grade Millwork (Saskatoon, SK), a by-product of their furniture manufacturing. A New Holland Model 770 forage chopper was used to reduce the particle size of the poultry litter. Separated flax shives were obtained with a suitable particle size and did not require size reduction. Drying of all samples was performed using the ABRI-Tech rotary dryer attached to the pyrolysis unit, and until moisture content was reduced to less than 10%.

2.3 Experimental Design and Methodology

A series of pyrolysis trials were designed to evaluate the effect of feedstock and operating conditions on the pyrolysis of agricultural and livestock residues. Due to the possibility that pyrolysis unit operation and product generation has a time bias (changes with time during operation), trials were performed prior to the experimental study with a baseline feedstock. Three feedstocks were selected according to a prioritization matrix (Section 3) for

comparison to the baseline hardwood sawdust feedstock. Three pyrolysis temperatures were evaluated: 400°C, 475°C, and 550°C for each feedstock. Due to differences in physiochemical properties of different feedstocks, it was not possible to achieve the design feeding capacity of the unit and the feeding rate varied between biomass types. The average feeding rates and percentage of design capacity is given in **Table 2.1** for all feedstocks. Random duplicates were performed during the study to determine reproducibility and error in the results.

2.1: Feeding Capacity and Rate

	Feeding Rate (kg/h)	Capacity (%)
Mixed Hardwood Sawdust	16.7	40
Wheat Straw	13.7	33
Poultry Litter	20.3	49
Flax Shive	11.9	29

2.4 Sample and Data Collection

Once the pyrolysis unit reached steady state operation, product samples of oil, char, and gas were collected for analysis. Operational procedures to ensure steady state operation were developed using the baseline feedstock. Oil and char samples were stored at 4°C prior to analysis.

In order to evaluate the mass and energy balance for the pyrolysis unit, the increase in oil and char mass over a 30 minute period was measured. The gas produced was calculated from the oil and char production and the total feed, assuming the total products equate the biomass input. Propane and electricity use was measured over the same 30 minute period.

2.5 Product Analysis

2.5.1 Characterization of Biomass

Biomass was characterized following the methods reported by Naik et al. (2009) and standards developed by ASTM International and the National Renewable Energy Laboratory (NREL). Proximate analysis was performed after the dried biomass samples were ground in a Wiley mill (to 0.5 mm):

- The moisture content of the biomass (after drying for pyrolysis) was determined using the procedure given in ASTM 3173-87. Biomass (3.0 g) was placed in an oven set to $105\pm 5^{\circ}\text{C}$ for 4 h and then cooled in a desiccator. This procedure was repeated until constant weight was observed.
- The ash content was determined in a laboratory muffle furnace (Holpack, USA) as per ASTM 3174-04.
- A 1.0 g sample of biomass was taken in a crucible and placed in the muffle furnace maintained at $575\pm 10^{\circ}\text{C}$ for 4 h. The crucible was removed from the furnace and placed in a desiccator. The above process of heating and cooling was repeated until constant weight was obtained and the fixed matter determined.
- The volatile matter in the biomass was determined by the procedure given in ASTM D 3175-07. A 1.0 g sample was taken and placed in a muffle furnace maintained at $950\pm 10^{\circ}\text{C}$ for 7 min. Then the crucible was removed from the furnace and placed in the desiccator. The loss of weight accounted for the volatile matter in the biomass.

The calorific values were determined in a static bomb calorimeter, a sealed Parr 1108, using an NREL method (NREL, 2005) and the detailed procedure described by Hubbard et al. (1956). Samples of 1.0 g were used for each analysis. Water (1.0 cm^3) was added to the bomb, which was then filled with oxygen (25-30 atm) at 25°C . The calorimeter was placed in an isothermal jacket with an air gap separation of 10 mm between all surfaces. The electrical energy for ignition was determined from the change of potential across a 1256 or 2900 mF capacitor when discharged from about 40 V through the platinum wire. The bomb calorimeter was submerged in a 10-calorimeter can filled with distilled water.

The chemical analysis of biomass samples was performed using CHNS (carbon, hydrogen, nitrogen, sulphur) elemental analysis. Furthermore, sugar composition was determined through NREL methods. The common organic elements such as C, H, N, S and O were analyzed in a Perkin Elmer Elementar CHNSO analyzer. C, H, N and S values were determined for each sample (4.0–6.0 mg) through combustion and detection of combustion products such as carbon dioxide, water, and nitric oxide within the apparatus. The percentage of oxygen was determined by means of difference.

For structural sugar analysis, the biomass was acid hydrolyzed for conversion of hemicellulose and cellulose to sugars following an NREL method (2005). Then, the sugar solution was neutralized with calcium carbide and analyzed using a Hewlett-Packard high

performance liquid chromatograph (HPLC) equipped with a refractive index (RI) detector and an Aminex HPX 87P column (BioRad, Hercules, CA) with a deashing guard cartridge (BioRad). Degassed HPLC- grade water was used as the mobile phase at the rate of 0.6 mL/min with an ambient column temperature (35°C). The injection volume was 20 μ L with a run time of 20 min. Calibration was carried out using mixed sugar standards of cellulobiose, glucose, xylose, galactose, arabinose and mannose. These standards were also used for quantification analysis by comparison of weight percentages. The acid insoluble part of the biomass was considered lignin.

2.5.2 Characterization of Bio-oil

The moisture content of the bio-oil was determined by Karl Fischer titration. The solid content was determined through filtration whereby 100 g of bio-oil was filtered by gravity and the remaining solids content was determined on a weight percent basis. The ash content was determined through incineration in a laboratory furnace at $575 \pm 10^\circ\text{C}$ for 4 h. Calorific value was determined through bomb calorimetry, as described in Section 2.5.1. However, cellulose thread was added between the platinum wire and sample to ensure combustion. This ensured combustion of the liquid sample. Correction factors were calculated. A sample calculation can be seen below. The viscosity was determined using a low viscosity (LV) cone and plate viscometer. A range of readings was taken at varying rotation speeds to extrapolate a viscosity for the liquid.

CHNSO analysis was performed by an Elementar analysis system. Gas chromatography (GC) analysis was carried out on a HP 5980 gas chromatograph equipped with a flame ionization detector (FID) and a 30 m \times 0.25 mm wall-coated open-tubular (WCOT) column coated with 0.25 mm film thickness of 5% diphenyl dimethyl siloxane supplied by J&W (DB-5). Helium was used as the carrier gas at a flow rate of 1.5 mL/min at a column pressure of 22 kPa. A small amount (0.2 μ L) of each sample was injected into the injection port of the GC using a split ratio of 50:1. Compound separation was achieved following a linear temperature program of 50 to 250°C (5°C/min), 250°C (20 min), so the total run time was 1 h. Percentage composition was calculated using a peak normalization method, with response factors used to correct detector response for oxygenated compounds. Each sample was analyzed twice in the GC and results were calculated as averages. The GC/MS (mass spectroscopy) analysis was carried out on a Varian Saturn 2200 GC/MS fitted with the same column and temperature programmed as the GC-FID. MS parameters were as follows: ionization voltage (EI) 70 eV, peak width 2 sec, mass range 40 to 500 amu, and detector voltage 1.5 volts. Peak

identification was carried out by comparison of the mass spectra with mass spectra available on National Institute of Standards and Technology (NIST-I and NIST-II) libraries. The compound identification was finally confirmed by comparison of their relative retention indices (RRI) with literature values (Vichi et al., 2007).

The retention times of the relevant products are set out in the Appendices. Furthermore, response factors (size of spectral peak proportional to the amount of the substance that reaches the detector in the GC instrument) of oxygenated and aromatic compounds were calculated through methods described by Dietz (1968). To determine the response factors of compounds with unknown response factors, these were mixed at a 1:1 ratio with a compound with a known response factor (hexane with a known response factor of 1) and the mixture was injected into the GC; the unknown response factor was calculated based on peak area differences. This was necessary as no detector responds equally to different compounds. These compounds are listed with retention times on the Appendices.

The chemical composition is commonly identified through chromatographic techniques such as GC and GC-MS. Different fuel characteristics such as calorific value, kinematic viscosity, density, water content, and pH can be documented. These techniques are commonly reported in the literature (Demirbas et al., 2007; Garcia-Perez et al., 2007; Oasmaa and Czernik, 1999; Rout et al., 2009; Sensoz et al., 2008; Sheu et al., 1988; Zhang et al., 2007).

The moisture content was determined by Karl Fischer titration. The solid content was determined through filtration whereby 100 g of bio-oil was filtered through gravity and the remaining solids content was determined on a weight percent basis. The pH was determined through both litmus paper and a pH meter for verification. The ash content was determined through incineration in our laboratory furnaces. The ash was also analyzed through ICP (inductively coupled plasma)-MS in order to determine inorganic compounds present. Calorific value was determined through bomb calorimetry similar to the method described above for biomass characterization. The viscosity was determined at 40°C using an LV cone and plate viscometer. A range of readings was taken at varying rotation speeds to extrapolate a viscosity for the liquid.

CHNSO analysis was performed using an Elementar analysis system. GC analysis was carried out on a HP 5980 gas chromatograph equipped with a flame ionization detector (FID) and a 30 m × 0.25 mm WCOT column coated with a 0.25 mm film thickness of 5% diphenyl dimethyl siloxane supplied by J&W (DB-5). Helium was used as the carrier gas at a flow rate

of 1.5 mL/min at a column pressure of 22 kPa. Each sample (0.2 mL) was injected into the injection port of the GC using a split ratio of 50:1. Compound separation was achieved following a linear temperature program of 50 to 250°C (5°C/min), holding at 250°C for 20 min, so the total run time was 1 h. Percentage composition was calculated using a peak normalization method, with response factors used to correct detector response for oxygenated compounds. Each sample was analyzed twice in the GC and results were calculated as averages. The GC/MS analysis was carried out on a Varian Saturn 2200 GC/MS fitted with the same column and temperature programmed as above. MS parameters were as follows: ionization voltage (EI) 70 eV, peak width 2 sec, mass range 40 to 500 amu, and detector voltage 1.5 volts. Peak identification was carried out by comparison of the mass spectra with mass spectra available on NIST-I and NIST-II libraries. The compound identification was finally confirmed by comparison of their relative retention indices (RRI) with literature values (Vichi et al, 2007).

The total acid number of samples was determined according to ASTM D D664-09a. This method expresses quantity base as milligram of potassium hydroxide per gram of sample that is required to titrate a sample in a mixture of toluene and propan-2-ol to which a small amount of water is added. For titration, a 0.1-mol/L alcoholic KOH solution (in propan-2-ol) is used. A sample size ranged from 0.10 to 0.25 g of sample was used for the titration. Titration was performed using a combination of an indicating electrode and a reference electrode (Ag/AgCl).

2.5.3 Characterization of Biochar

Ash and moisture contents of the biochar were analyzed through procedures similar to those described for biomass in 2.5.1. CHNSO analysis was performed on an Elemental analysis system. Calorific value was determined through bomb calorimetry similar to the method described above for biomass characterization.

The Brunauer-Emmett-Teller (BET) surface area and total pore volume of the biochar samples were analyzed by adsorption-desorption of N₂ at 77 K in a Micrometrics 2000 ASAP analyzer. A 0.05 gram quantity of each sample was degassed for 2 h under vacuum conditions and a temperature of 200°C. The physical characteristics of each sample were determined using the procedure developed by BET (Gregg et al., 1977). The pH of samples was determined according to ASTM D 3838-80. A 10.00 g sample was weighed on a dry basis. This sample was added into a 250 ml Erlenmeyer boiler flask. Boiling water (100.0

mL) was added to the carbon in the flask. The water in the flask was brought to a boil on a hot plate using thermometer readings (to $\sim 110^{\circ}\text{C}$) and was boiled gently for 900 s. The flask was removed from the hot plate and its contents were filtered immediately through a filter paper pre-moisturized with the distilled water. Then, 50.0 mL of filtrate was poured in a flask with care to prevent carbon-fines from overrunning into the flask. The filtrate was cooled. pH measurement was performed by pH meter. Particle size distribution was determined based on laser beam diffraction pattern of particles, using the Malvern Mastersizer S Long Bench particle size analyzer (Malvern instruments Ltd., Malvern, UK) using a wet method and the 300 mm: 0.50–880 μm lens.

2.5.4 Characterization of Gases

GC analysis was carried out using a Varian CP-3800 gas chromatograph equipped with a flame ionization detector (FID) and a 30 m / 0.25 mm column coated with 0.25 μm film thickness (DB-5 column). Helium was used as the carrier gas at a flow rate of 1.2 mL/min at a column pressure of 22 kPa. Each sample was injected into the injection port of the GC using a split ratio of 50:1. Compound separation was achieved following a linear temperature program of 50– 250 $^{\circ}\text{C}$ ($5^{\circ}\text{C}/\text{min}$) then 250°C . The total run time was 45 minutes. The percentage composition was calculated using the peak normalization method. Each sample was analyzed twice in the GC and results were calculated as averages.

2.6 Changes in Original Project Plan

Changes were made to the original project plan over the course of the project. These are as follows:

- A mobile test of the pyrolysis unit was originally planned; however, this has been delayed until summer 2011. This task was removed from the immediate task list when:
 - it was determined that the unit is in fact not truly standalone and therefore not fully mobile
 - the cold weather between December 2010 and February 2011 inhibited pyrolysis unit operation and an outside demonstration
 - the time and effort required to employ a new feedstock made it impractical to do a field test without detailed work on a feedstock of identical properties first

- A fourth feedstock [wheat DDGS (dried distiller's grains with solubles)] was intended to be included but was eliminated due to time constraints and difficulty in determining a method whereby it could be pyrolyzed in the existing unit.

2.7 Results Dissemination

In addition to reporting the complete study results to ADF, the project concept and results were disseminated as follows:

- A brief paragraph on the project in an article on pyrolysis written as part of the International Energy Agency's (IEA) Task 39.
- Presentation of the results at the Biomass '11 conference in Grand Forks, ND, in July 2011.
- Inclusion of project profile in factsheets at SRC booth at 2011 International Biomass Conference and Expo, St. Louis, MO, in May 2011.
- Demonstration of mobile pyrolysis unit and testing at a rural location in summer 2011.
- Training of highly qualified personnel in the form of a post-doctoral fellow and a M.Sc. graduate student. This activity has resulted in dissemination of the work as part of a thesis and publications, as well as training students within Saskatchewan in this field.

3. PRIORITIZATION OF AGRICULTURAL FEEDSTOCKS

3.1 Selection of Feedstocks for Consideration

A variety of Saskatchewan agricultural and livestock residues were evaluated as candidates in order to assess this mobile auger pyrolysis technology. These were selected from three categories of residues: agricultural, livestock, and agri-food processing. The residues include wheat straw, wheat chaff, canola straw, rye straw, barley straw, flax straw, hay, hog manure, dairy manure, beef manure, poultry litter, oat hulls, DDGS, and canola meal. These were evaluated based on a set of criteria of varying importance to the project. The three feedstocks with the higher rating using the prioritization matrix were selected for the study.

3.2 Prioritization Criteria and Importance

The criteria used to evaluate the feedstocks are presented in Table 3.1. The relative importance of each criterion is assessed (see Appendices) as a factor of both the importance to the project and the priority relative to the null condition.

3.1: Feedstock Evaluation Criteria

Criterion	Measure	Definition
Low Value of Feedstock	Low to High	Value of feedstock if sold as agricultural/livestock residue to producers (for any use)
High Volume of Feedstock Produced	Low to High	High volumes are produced as a by-product of agriculture/livestock being readily available and accessible for use
Disposal Difficulty/Cost of Feedstock	Low to High	Difficulty/cost level for producers to dispose of residue
Environmental Concerns of Feedstock	None to Significant	Any environmental concerns with traditional use/disposal of residue
Market for Technology if Feedstock Selected	None to Significant	Future markets for mobile pyrolysis technology if proven for use with particular feedstock
Fit to Technology	Low to High	Suitability of feedstock for use with selected mobile pyrolysis technology
Feedstock Collection	Low to High	Ease of access and <i>inexpensive</i> to obtain feedstock for pyrolysis trials
Public Perception	Low to High	Perception by producers that the residue would make a good feedstock for pyrolysis for any of the other listed reasons
Additional Pre-processing requirements	High to Low	Additional pre-processing required for use with pyrolysis unit (i.e., grinding, drying, special handling, leaching)
Potential for High-value End-Use - Oil	Low to High	Potential use for char end products from this feedstock, upgraded or not
Potential for High-value End-Use - Char	Low to High	Potential use for oil end products from this feedstock, upgraded or not

3.3 Results of Prioritization Matrix

The four feedstocks that produced the highest priority weight are summarized in **Table 3.2**. These values take into account both relative importance of each criterion and the individual rating for each criterion for each feedstock.

3.2: Maximum Results of Prioritization Matrix

Feedstock Options	Wheat Straw	Flax Straw	Poultry Litter	DDGS
Project Needs and Requirements				
Low Value of Feedstock	3	6	7	2
High Volume of Feedstock Produced	9	1	5	3
Disposal Difficulty/Cost of Feedstock	2	6	7	2
Environmental Concerns of Feedstock	1	3	5	1
Market for Technology if Feedstock Selected	4	3	5	4
Fit to Technology	5	3	4	8
Feedstock Collection	5	5	8	9
Public Perception	3	6	8	1
Additional Pre-processing Requirements	6	4	4	9
Potential for High-value End-Use - Oil	3	3	3	4
Potential for High-value End-Use - Char	3	3	3	5
Requirement Weight	428	448	594	520
Relative weight (%)	7.2	7.5	10.0	8.7

Although prioritization involves many factors, there were key factors that increased the value of certain feedstocks to the study. Wheat straw is particularly desirable due to its abundance in the province, making it readily available and present in great excess in certain crop years.

Canada is the fourth largest producer of wheat in the world (Naik et al., 2009). It is also obtained for use in a reasonably dry state and is easy to grind, making pre-processing relatively simple. Wheat straw has already been used successfully as a raw material in the renewable energy sector (Naik et al., 2009). Canada is the largest producer and exporter of flax seed (Government of Saskatchewan, 2010), although the total production is significantly less than that of wheat. Flax produces a straw at harvesting that is still frequently simply burned on the field as a residue management practice. Unlike other straw like wheat, flax straw is problematic in regards to being tilled under the soil for enrichment. The fibre fraction of the straw has value, as it can be used in linen, twine and rope production, as well specialty papers. This requires separation from the shive fraction, which has minimal use in North America, making it more frequently more practical for farmers to waste it in burning. Flax straw has been used successfully for bio-fuel production, as it has a per tonne heating value similar to that of coal (Naik et al., 2009). Poultry litter does possess a market as a fertilizer; however, due to public perception and environmental concerns that it is not as valuable or safe as other fertilizers, this market is limited. Poultry litter is also the feedstock for which the ABRI pyrolysis unit was designed, and is therefore excellent for evaluating the unit. DDGS made from wheat during fermentation to ethanol is readily available in Saskatchewan, with a mandate for more ethanol production in the future. At present DDGS has a strong market as an animal feed; however, with increased production the price and demand may fall and excess DDGS will need management. Also, ethanol fermentation plants are energy intensive, making the benefits of pyrolysis of DDGS for on-site use attractive.

4. MOBILE PYROLYSIS UNIT

4.1 Commissioning

The commissioning of the 1 dry tonne per day portable pyrolysis unit was originally begun in 2010, using mixed hardwood shavings as the baseline feedstock. Commissioning and operational testing required several months as it was determined that there were several issues with the design as manufactured that needed to be addressed. Several factors have significant effects on the operation of the pyrolysis unit: unit flexibility, unit design, feedstock type, cold weather, and wide range of operating temperatures.

4.2 Modifications and Troubleshooting

It was determined that there were issues with char carryover to the bio-oil collection system, and the manufacturer suggested using their recently developed design modification. Modifications based on the manufacturer's suggestion were made and operating tests continued. During the commissioning and operational testing, other design issues emerged, including bio-oil pump failure, bio-oil sampling tube blockage, water fall blockage, dried biomass feeding auger obstruction and failure, venturi condenser blockage, demister outlet pipe blockage, and dryer flails blockage. Modifications and repairs to the original design were ongoing to deal with these issues. A novel design for the bio-oil sample collection system had to be developed, as this was lacking in the pyrolysis unit as received, but was successfully completed. Char carryover continued to be a problem, as the new design configuration proposed by the manufacturer did not work as intended. Poor shot quality and circulation (used for mass transfer inside the system) and char and shot separation continued to be major issues.

Based on collected experimental data during commissioning, it was found that the unit could operate productively at 30 to ~40% of its stated manufacturer design capacity. At a greater feedstock input rate, problems occurred throughout the pyrolysis unit system. Major modifications were made to the unit's design by SRC and testing continued over several months. The pyrolysis unit can now be operated continuously for a full day.

In addition, the desire to study a wide range of operating temperatures is a significant issue. Char yield (and high temperature vapour) is a function of the operating temperature. As a result, the separation efficiency of char and shot will vary for each temperature. Poor separation efficiency can result in a blockage of the entire system, which can be dangerous.

4.3 Challenges to Pyrolysis of Feedstocks

Although the pyrolysis unit was meant to be used for a variety of biomass feedstocks, it was designed with poultry litter in mind. Although this unit might be suitable for the feedstock tested by the manufacturer, it was proven that it could not reach its designed capacity for other feedstocks, even the specific poultry litter used in this study. When other feedstocks were attempted, there was always a confounding problem, such as a feed auger jam or flails jam, even with size reduction beyond the 1/8 inch (in one dimension) required by the manufacturer. The manufacturer indicated that a single feedstock dimension of less than 1/8 inch was suitable for pyrolysis with this unit; however, with fast pyrolysis, a finely ground biomass feed is normally required for high heat transfer rates (Mohan et al., 2006)

Cold weather was the second major issue. There were several times that the pyrolyzer could not reach its desired operating temperatures due to the extremely cold ambient temperature outside. Other times, although the unit reached the operating temperature, this temperature dropped sharply after feeding of feedstock from outside. As well, in very cold weather the unit was difficult for staff to operate safely and efficiently, as observed in **Fig. 4.1**. These difficulties are not insurmountable, but require ongoing pyrolysis unit modifications to remedy these difficulties. Improvements to the current unit could resolve these problems.



Fig. 4.1: Unit operations in inclement winter weather.

5. PYROLYSIS OF FEEDSTOCKS

5.1 Characterization of Biomass

5.1.1 *Mixed Hardwood Sawdust: Baseline Feedstock*

Fundamental characterization of biomass is imperative, as the chemical composition of biomass affects conversion processes differently. Rout et al. (2009) proposed characterization through chemical and physical means for the determination of the heating value, ash content, volatile matter, elemental composition, and amounts of key components (cellulose, hemicellulose, and lignin) in the biomass. A baseline feedstock of mixed hardwood sawdust was made up of shavings from a variety of hardwoods such as maple, oak, and birch. A photograph of the sawdust as received is shown in **Fig. 5.1**. The average particle size is 3 mm; the particle size distribution is presented in **Table 5.1**, with a detailed particle size distribution provided in the Appendices. Aguiar et al. (2008) studied the effects of temperature and particle size of orange peel residue in a fixed bed pyrolysis reactor. They concluded that, during the pyrolysis process, temperature plays a much more significant role in product formation than particle size.

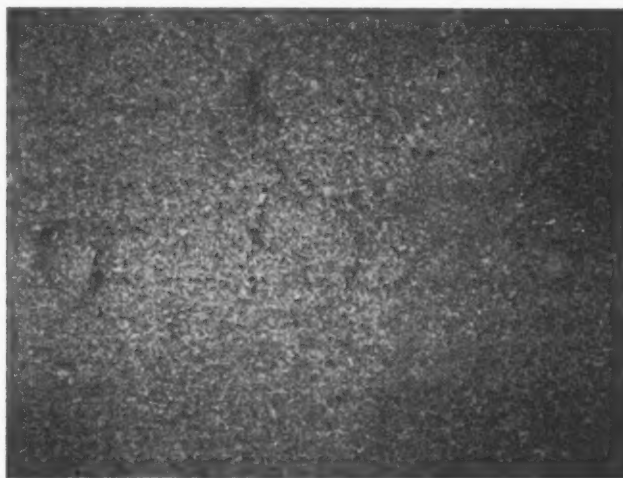


Fig. 5.1: Hardwood sawdust.

5.1: Particle Size Distribution of Mixed Hardwood Sawdust

Particle size	weight%
>3.36 mm	48.3%
2.00–3.36 mm	15.8%
1.41–2.00 mm	9.8%
0.840–1.41 mm	11.6%
0.595–0.840 mm	6.2%
0.425–0.595 mm	2.2%
<0.425 mm	6.0%
Total sample	100.0%

The proximate and ultimate analyses of the sawdust are provided in **Tables 5.2 and 5.3**. These results are consistent with the findings of Rout et al. (2009). The moisture content of the sawdust at 6.2 wt% was ideal for baseline trials, as the feedstock did not require further drying before pyrolysis. This very low moisture content could be due to air drying of the wood during processing and storage. The heating value of the mixed hardwood sawdust was determined to be 19.5 MJ/kg \pm 0.2 MJ/kg. This agrees with values for hardwoods reported in Hearth (2011).

5.2: Proximate Analysis of Mixed Hardwood Sawdust

Moisture	Ash	Volatile Matter	Fixed Matter
6.2%	1.4%	81.7%	10.7%

error = 0.2

5.3: Ultimate Analysis of Mixed Hardwood Sawdust

C	H	N	S	O
44.6%	6.6%	0.01%	0.01%	48.8%

The composition of the sawdust is provided in **Table 5.4**. At first glance it seems unusual that the mixed wood contains relatively little lignin, as wood is a strong and rigid plant structure. However, sawdust is not simply whole wood made into small particles; it is a product of cutting lumber and may contain an uneven distribution of the components of wood depending on the manufacturing project. However, analysis on pinewood sawdust performed by Naik et al. (2009) and on birch by Mohan et al. (2006) agrees with these results for mixed wood. For whole wood species, Sjostrom (1993) found that hardwoods such as birch contain less lignin than softwoods such as pine and spruce.

5.4: Composition of Mixed Hardwood Sawdust

Cellulose	Hemicellulose	Lignin	Extractives
37.7%	31.4%	15.9%	15.0%

error = 1.8

5.1.2 Wheat Straw

The wheat straw used in the pyrolysis trials is shown in **Fig. 5.2**. This feedstock was easy to grind, dry and pyrolyze. After grinding the average particle size was 1.7 mm, smaller than the baseline sawdust. The particle size distribution is provided in **Table 5.5**. The heating value for the unpyrolyzed wheat straw was 19.8 MJ/kg \pm 0.2 MJ/kg. This agrees with the work of Naik et al. (2009).

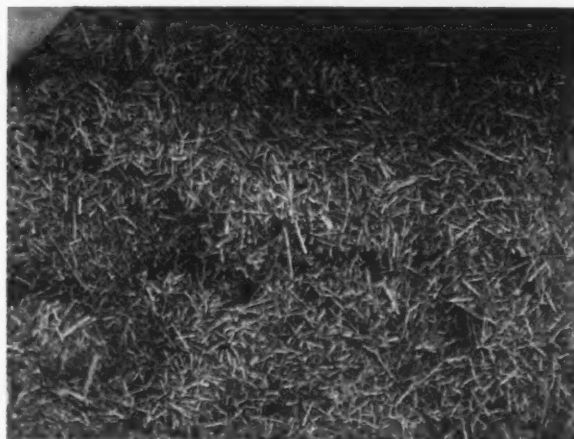


Fig. 5.2: Wheat straw.

5.5: Particle Size Distribution for Wheat Straw

Particle size	weight%
>3.36 mm	4.9%
2.00–3.36 mm	29.1%
1.41–2.00 mm	26.5%
0.840–1.41 mm	21.4%
0.595–0.840 mm	10.3%
0.425–0.595 mm	3.2%
<0.425	4.4%
Total sample	99.9%

The characterization of the wheat straw feedstock is provided in **Tables 5.6, 5.7, and 5.8**. The proximate and ultimate analyses agree closely with the findings of Naik et al. (2009). A high percentage of carbon and volatile matter, and a low ash, sulphur and nitrogen content, are considered desirable in a feedstock for pyrolysis (Scott et al., 2009). It has been reported that agricultural residues such as straw tend to have lower moisture contents (Tushaw et al., 2010; Wang et al., 2010) making them ideal for processes like pyrolysis.

5.6: Proximate Analysis of Wheat Straw

Moisture	Ash	Volatile Matter	Fixed Matter
6.3%	1.3%	78.4%	14.0%

error = 0.2

5.7: Ultimate Analysis of Wheat Straw

C	H	N	S	O
44.8%	6.1%	0.1%	0.02%	49.0%

The composition of wheat straw varies with species variety, with the values in **Table 5.8** falling within the range reported by Antongiovanni and Sargentini (1991). This corresponds closely to the wheat straw characterization performed by Naik et al. (2009). As is expected of a straw, the feedstock contains a high amount of cellulose. It also contains a significant amount of lignin, normally considered undesirable for pyrolysis due to the resulting phenols in the oil and greater resulting char. The extractives present include non-polar lipids; hydrocarbon compounds; terpenoids; polar compounds such as chlorophyll, polar waxes, and sterol; inorganic materials; and non-structural sugars.

5.8: Composition of Wheat Straw.

Cellulose	Hemicellulose	Lignin	Extractives
35.4%	29.7%	20.8%	14.1%

5.1.3 Poultry Litter

The poultry litter used in the pyrolysis trials is shown in **Fig. 5.3**. This litter required more extensive drying than the other feedstocks and was difficult to reduce in size and feed into the pyrolysis unit, as it tends to clump together. It was also had a foul odour, particularly while drying. The repeatability error (5%) for the poultry litter analysis was greater than for other samples due to the heterogeneous aspects of the mixed feces, urine, bedding, as well as small amounts of dirt, spilled feed and feathers. After grinding, the average particle size was 0.9

mm. The particle size distribution is provided in **Table 5.9**, with detailed data in the Appendices. The heating value for the unpyrolyzed poultry litter was $23.2 \text{ MJ/kg} \pm 0.2 \text{ MJ/kg}$. This is significantly higher than the heating value of 13 MJ/kg for poultry litter reported by Ro et al. (2010) and Singh (2007). Poultry litter decomposes during long storage, resulting in a reduced heating value (Singh et al., 2007). Also, the bedding used in poultry litter varies greatly, from straw of various types, to woods chips, to old paper products, affecting the total heating value of the combined poultry litter.



Fig. 5.3: Poultry litter.

5.9: Particle Size Distribution for Poultry Litter

Particle size	weight%
>3.36 mm	1.8%
2.00–3.36 mm	5.8%
1.41–2.00 mm	6.8%
0.840–1.41 mm	17.2%
0.595–0.840 mm	11.7%
0.425–0.595 mm	25.0%
<0.425	31.4%
Total sample	99.9%

The characterization of the poultry litter feedstock is provided in **Tables 5.10, 5.11, and 5.12**. It has the highest moisture content of all feedstocks, partially due to the difficulty in drying it well. Increasing the moisture content of the feedstock can increase the resultant char and gas yields (Westerhof et al., 2007). A significant fraction of any biomass consists of inorganic constituents, referred to as ash, which can rarely be converted into energy. The ash content

of the poultry manure is particularly high relative to the other feedstocks, a finding that corresponds to Agblevor et al. (2010) and Ro et al. (2010), as well as other manure feedstocks. Agblevor et al. (2010) found that these relatively large fractions of ash are rich in potassium, phosphorus, calcium, and magnesium, and can be pyrolyzed at higher temperatures (450–550°C) to produce a viscous brown bio-oil.

5.10: Proximate Analysis of Poultry Litter

Moisture	Ash	Volatile Matter	Fixed Matter
10.2%	12.3%	68.4%	9.0%

error = 0.2

The ultimate analysis of the poultry litter feedstock agrees primarily with the data of (Schnitzer et al., 2007a), except that the ratio of carbon to oxygen is significantly higher. The composition is similar to that of wheat straw, as wheat straw is a major component of the litter. The poultry litter possessed the highest ash content, 12.5 wt%, highest nitrogen content, 3.9 wt%, and highest calorific value, 24.3 MJ/kg than the other evaluated feedstocks. However, the calorific value was slightly less than the predicted value of 26 to 29 MJ/kg reported by Agblevor et al. (2010). The lower heating value in the present study could be due to the raised moisture content and/or soil content in the litter. The composition of the litter in Table 5.12 demonstrates a lower proportion of cellulose, hemicellulose, and lignin than in the other feedstocks, as expected due to the presence of feces in the litter.

5.11: Ultimate Analysis of Poultry Litter

C	H	N	S	O
44.4%	5.7%	3.9%	0.4%	45.6%

5.12: Composition of Poultry Litter

Cellulose	Hemicellulose	Lignin	Extractives
31.2%	36.3%	15.6%	16.9%

5.1.4 Flax

As discussed in Section 1, flax straw is made up of both a woody shive fraction and a flexible fibre fraction. Well-retted flax separates into the two distinct types during grinding, as shown in Fig. 5.4. This material can be pyrolyzed as a whole or separated into the two fractions, with the fibre going to other products, and the shive being pyrolyzed. The separated flax

shive is shown in **Fig. 5.5**. The presence of the fibre in the ground flax proved very problematic for pyrolysis. The properties of the long elastic flax fibres resulted in clumping, burning, and plugging inside the augers of the pyrolysis unit. Due to the inability to solve these problems without a full unit redesign, or special handling of the fibre not presently available at SRC, only the shive fraction was used for the trials, with the assumption that the fibre fraction can be used for more valuable products.



Fig. 5.4: Whole chopped flax, with fibre and shive fractions mixed together.



Fig. 5.5: Separated flax shive.

After grinding, the average particle size was approximately 1.0 mm; the particle size distribution is provided in **Table 5.13**. Flax was analyzed in three separate fractions: whole flax straw consisting of the whole flax stalk; flax straw/shive consisting of the exterior of the stalk and “woody” material within the stalk; and flax fibre consisting of the long string-like inner material. The heating values for unpyrolyzed flax are given in **Table 5.14**. The heating value of whole flax straw is similar to that of coal (Naik et al., 2009).

5.13: Particle Size Distribution for Flax Straw (Shive Only)

Particle size	weight%
>3.36 mm	0.2%
2.00–3.36 mm	3.2%
1.41–2.00 mm	13.3%
0.840–1.41 mm	30.5%
0.595–0.840 mm	26.3%
0.425–0.595 mm	7.2%
<0.425	19.3%
Total sample	99.9%

5.14: Heating Values of Flax Straw Fractions

	Heating Value (MJ/kg)
Whole Straw	18.8
Shive Only	17.2
Fibre Only	16.7

error = 0.2

The characterizations of flax straw and its fractions are provided in **Tables 5.15, 5.16, and 5.17**. The above results are in agreement with those reported in literature. Flax straw contains significant lignin (Ross and Mazza, 2010) and Naik et al. (2009) found the lignin content in the flax straw to be 22.5%, as reported in Table 5.17. Sain and Fortierb (2002) reported significantly higher cellulose content in flax, perhaps as their straw was unretted. Li (2008) found that flax fibre had the highest cellulose and the lowest lignin content of the flax straw fractions. As the shive content increased, lignin content also increased. Flax shive contained more lignin and hemicellulose, and less cellulose, than pure flax fibre. These observations are in agreement with the data Table 5.17. From these data, it can be concluded that the shive contains the most lignin, whereas the fibre contains the most cellulose. The ultimate analysis of flax straw indicates an almost identical distribution of organic elements as wheat straw.

5.15: Proximate Analysis of Flax Straw

	Moisture	Ash	Volatile Matter	Fixed Matter
Whole Straw	10.3%	1.9%	77.4%	10.4%
Shive Only	8.1%	3.1%	79.9%	8.9%
Fibre Only	6.9%	5.7%	76.4%	11.0%

error = 0.2

5.16: Ultimate Analysis of Flax Straw

	C	H	N	S	O
Whole Straw	45.8%	6.3%	0.1%	0.01%	47.8%
Shive Only	46.3%	6.2%	0.1%	0.01%	47.4%
Fibre Only	46.2%	6.3%	0.1%	0.01%	47.4%

5.17: Composition of Flax Straw

	Cellulose	Hemicellulose	Lignin	Extractives
Whole Straw	35.1%	29.2%	21.3%	14.4%
Shive Only	32.3%	27.5%	20.1%	20.1%
Fibre Only	48.1%	17.2%	12.0%	22.7%

error = 1.8

The present analysis confirms the findings in the literature, noted before the tables. It was observed that the flax shive contained 20.1 wt% lignin, which is significantly larger than the lignin content of the fibre, 12.0 wt%. Furthermore, the flax fraction had a greater content of cellulose, 48.1 wt%, when compared with the cellulose content of the flax straw, 32.3 wt%. The straw/shive of the flax, which is described as "wood-like" and is also a strong and rigid plant structure, contains a high amount of lignin. If the fibre were separated prior to pyrolysis, cellulose would be lost, and the higher lignin content of the straw and shive would contribute to more phenolics within the bio-oil (Section 2.3.1).

5.1.5 DDGS

It was intended to perform a fourth set of trials using wheat DDGS as a feedstock. A sample of the feedstock is shown in Fig. 5.6. Pyrolysis of the wheat DDGS proved problematic due to the presence of very hard large aggregate particles within the sample. These aggregates are a result of the drying process and resulted in plugging when heated within the pyrolysis reactor. It may be possible to overcome this problem by first milling the DDGS aggregates into a very fine particle; however, due to time and equipment constraints, work with DDGS was deferred for the present.

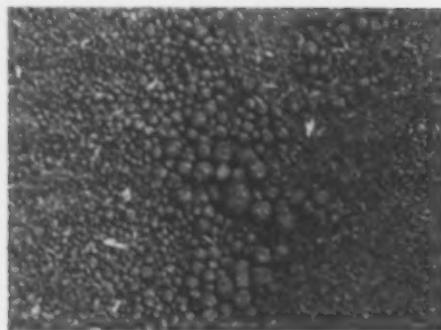


Fig. 5.6: Large hard particles in wheat DDGS.

6. RESULTS AND DISCUSSION

6.1 Pyrolysis of Agricultural and Livestock Feedstock

6.1.1 Justification for Baseline

Baselining is gathering of information at the beginning of a study from which variations found in the study are measured. Unknown or new data are compared when measured or assessed to this known baseline value. Mixed hardwood sawdust was selected to serve as the baseline feedstock. It is readily available, in a dry form with small particle size, and significant literature exists for comparison on pyrolysis of this material including its properties and products.

6.1.2 Results of Pyrolysis Trials

The results of the pyrolysis trials are summarized in **Tables 6.1 to 6.8**. As well, when such context provides insight, they are compared with relevant results from the literature.

6.1: Distribution of Products of Pyrolysis of Sawdust

Temperature (°C)	Percentage of Total Products Produced		
	Oil	Char	Gas
400	38	15	48
475	57	17	26
550	23	11	66

6.2: Distribution of Products of Pyrolysis of Wheat Straw

Temperature (°C)	Percentage of Total Products Produced		
	Oil	Char	Gas
400	51	35	14
475	45	36	19
550	16	32	52

6.3: Distribution of Products of Pyrolysis of Poultry Litter

Temperature (°C)	Percentage of Total Products Produced		
	Oil	Char	Gas
400	52	34	14
475	43	33	24
550	50	26	24

6.4: Distribution of Products of Pyrolysis of Flax

Temperature (°C)	Percentage of Total Products Produced		
	Oil	Char	Gas
400	49	23	28
475	36	27	37
550	45	19	36

The expected typical distribution of products, based on information provided by Dr. Peter Fransham of ABRI-Tech Inc.(manufacturer of pyrolysis technology used in present study), is 60 wt% liquid bio-oil, 20 wt% solid bio-char and 20 wt% off-gas. However, although liquid yields of 57% were observed, the char and gas yields reached 36% and 66%, respectively. A lower ratio of oil to char similar to that observed here has been observed in other studies (Brown et al., 2010), with char at 15 to 40% and oil at 40 to 55%. Putun et al. (2005) and He et al. (2009) also observed a significantly lower range of oil products, which is more similar to those presented in this study. Agricultural residues (straws and grass) possess high lignin contents and may therefore produce lower liquid yields and higher char yields. Char production is also increased by feedstock moisture content, which was highest for poultry litter, as was ash content, which also contributes to char production. As well, although the pyrolysis unit being assessed is designed for fast pyrolysis, the low bio-oil production and modifications required for improved operation indicate that this unit does not in fact carry out "fast" pyrolysis, but rather pyrolysis with a significantly longer residence time.

A trend of decreasing char yield and increasing gas yield with increasing temperature was observed for some feedstocks, which is in agreement with literature reports. Putun et al. (2005) and Aguiar et al. (2009) also observed that as temperature increased, char yield decreased, while liquid and gas yields increased. Putun et al. (2005) suggested that the increase in gas yield was caused by a secondary reaction of the pyrolysis vapours in the reactor. The decrease in the char yield with increasing temperature was attributed to either greater primary decomposition of biomass at higher temperatures or to secondary decomposition of char residue into gas and tar. The secondary decomposition of the char at

higher temperatures may also give some non-condensable gaseous products, which would also contribute to an increase in gas yields.

There was no significant observable trend of temperature on total oil production except for wheat straw. All feedstocks had oil production at the lower ranges of those reported in the literature. In the case of wheat straw the effect was of a decrease in oil production with increasing temperature. He et al. (2009) reported that same phenomenon.

The char production was highest for wheat straw and poultry litter. In the case of wheat straw, that higher char production can be explained by the high lignin content (He et al., 2009). Agblevor et al. (2010) showed that the high ash content of poultry litter is directly related to the amount of char produced, and consequently bio-oil yields were relatively low for poultry litter, with final products depending on the age and bedding material content of the litter (with respect to contaminants such as dirt affecting pyrolysis). The ratios of products observed with the pyrolysis of poultry litter in this study are similar to those observed by Singh (2007) for poultry litter.

Westerhof et al. (2007) concluded that increased moisture content results in increased char and gas yields. It has been theorized that the increase in char yield is a result of the extra moisture lowering the effective pyrolysis temperature of the particles (as distinct from the reactor temperature of the unit). There is no experimentally confirmed explanation for the increase in gas yield, although it has been suggested that the additional water furthers the gasification reaction of char (Chen and Andries, 2001). This could be a reason for the higher char and gas yields observed in the SRC study relative to those predicted by Dr. Peter Fransham of ABRI-Tech Inc. Although all biomass was dried to 10% moisture or less, the separation of the dryer and the reactor skids on the trailer provides opportunities for exposure to additional moisture, particularly in inclement weather. As well, the larger particles suitable for an auger style reactor retain internal bound moisture not readily measured.

The distribution of products can also be markedly affected by an inadequate heat transfer (Scott et al., 1988). The quality of heat transfer in the current pyrolysis unit design was also a concern in this project.

Also, the reported distribution of products assumes that the total gas produced closes the mass balance for a total product yield of 100%. This was necessary, as measurement of the gas produced was not possible in the present pyrolysis unit configuration. In actuality, losses

of 10% or higher have been reported in pyrolysis mass balances (Czernik et al., 1994), which would alter the yield ratios as calculated, and impacts the error in the gas yield values.

6.5: Energy Consumption during Pyrolysis of Sawdust

Temperature (°C)	Propane Consumption (kg/h)	Electricity Consumption (kWh)
400	2.1	7.2
475	2.3	5.4
550	2.8	6.8

6.6: Energy Consumption during Pyrolysis of Wheat Straw

Temperature (°C)	Propane Consumption (kg/h)	Electricity Consumption (kWh)
400	2.0	7.6
475	2.0	7.7
550	2.9	7.8

6.7: Energy Consumption during Pyrolysis of Poultry Litter

Temperature (°C)	Propane Consumption (kg/h)	Electricity Consumption (kWh)
400	2.6	6.0
475	2.7	6.0
550	3.6	5.2

6.8: Energy Consumption during Pyrolysis of Flax

Temperature (°C)	Propane Consumption (kg/h)	Electricity Consumption (kWh)
400	2.6	7.6
475	2.6	7.7
550	3.0	7.7

As expected, the energy usage, in the form of propane, increased with increasing pyrolysis temperature from 400°C to 550°C. The increase is not necessarily linear, as it was impacted by the ambient temperature outside. The energy values can be significantly affected by the weather due to outdoor operation resulting in a much higher error. The electricity usage is not significantly different between the trials, given the error associated with the results. The electricity used per run is essentially constant between temperatures and trials, as electricity

is used to operate systems not significantly dependent on feedstock or temperature, such as computer and monitoring equipment and fans.

6.2 Characterization of Pyrolysis Products

6.2.1 Oil

Bio-oil samples collected from the mobile pyrolysis unit were a mixture of an aqueous phase and a non-aqueous phase. Each sample was separated into two phases and analyzed; one lighter aqueous fraction, and one heavier organic fraction. Although simple removal of the aqueous phase seems desirable to reduce the water content, a significant portion of the oil's organics can be lost to the aqueous phase (Westerhof et al., 2007); therefore both fractions must be considered in evaluating the total oil product. The separation of the oil fractions for each feedstock and temperature are provided in **Table 6.9**.

6.9: Fractional Separation of Oils

	Temperature (°C)	Fraction 2: Heavy Fraction	Fraction 1: Light Fraction
baseline	400	0.00*	1.00
	475	0.65	0.35
	550	0.53	0.47
wheat straw	400	0.15	0.85
	475	0.32	0.68
	550	0.62	0.38
poultry litter	400	0.56	0.44
	475	0.54	0.46
	550	0.36	0.64
flax shive	400	0.36	0.64
	475	0.4	0.6
	550	0.59	0.41

*single oil fraction only

6.2.1.1 Moisture Content

The moisture contents of the pyrolysis oils are high, as observed in **Tables 6.10 and 6.11**. The water content is very high in the collected bio-oil samples, and is significantly lower in the heavy organic fraction alone. These high water contents in the heavy fraction correspond to results in Oasmaa and Czernik (1999). Water content varies widely in bio-oils based on feedstock and process conditions. Water content is derived from the initial moisture in the

feedstock and dehydration during pyrolysis and storage (Qi et al., 2008). As well, the decreasing trend in water content in Fraction 2 observed with increasing temperature for pyrolysis oils agrees with He et al. (2009). The higher water contents of the pyrolysis oils in this study may also be partially due to storage at 4°C, with some aging occurring. Pyrolysis oil water content has also been shown to be affected by the condenser temperature, particularly in the range of 35 to 70°C, with higher condenser temperature resulting in greater water in the collected oil (Westerhof et al., 2007). However, water removal using condenser temperature is accompanied by loss of some organic vapours by entrainment with the gas stream.

6.10: Properties of Oil from Pyrolysis of Sawdust

Temperature (°C)	Water Content – Total Oil (%)	Water Content – Fraction 2 (%)	Water Content – Fraction 1 (%)
400	56.0	-	56.0*
475	37.3	17.6	73.9
550	48.9	13.6	88.8

error 2.2%

*one fraction only

6.11: Moisture Content of Pyrolysis Oils

	Temperature (°C)	Water Content – Total Oil (%)	Water Content – Fraction 2 (%)	Water Content – Fraction 1 (%)
Wheat Straw	400	77.2	35.6	84.5
	475	69.9	38.3	84.8
	550	52.1	27.3	92.6
Poultry Litter	400	49.9	23.5	83.4
	475	50.8	20.4	86.4
	550	64.2	16.1	91.3
Flax Shive	400	69.1	33.3	89.2
	475	63.7	20.7	92.4
	550	49.3	18.9	93.1

error 2.2%

6.2.1.2 Total Acid Number

Total acid number provides information on the acidity of materials, indicating the concentration of acidic constituents in the oil. The values in **Tables 6.12 and 6.13** indicate a decrease in acidity with increasing temperature. The values measured in this study are high. He et al. (2009) reported that the acidity of the bio-oil that they studied could be slightly reduced by increasing the process temperature to 550°C. These values are an indication of the corrosiveness of the oil, with acid numbers of 50 to 100 (similar to those observed in this

SRC study) being the typical range [corresponding roughly to pH values of 2–3 (Oasmaa and Czernik, 1999)]. Poultry litter oils exhibited the lowest acid numbers of all samples, possibly due to the impact of the higher ash content. Agblevor et al. (2010) found that these relatively large fractions of ash can be pyrolyzed at higher temperatures (450–550°C) to produce a viscous brown bio-oil with less acidic pH of 6.

The total acid number is used in oil field analysis to estimate the amount of additive depletion, acidic contamination, and oxidation (by measuring by-products of oxidation) of samples, particularly as they age. The high acid numbers measured in the present study indicate that oil treatment and upgrading is required to create a usable fuel product. The acidity of pyrolysis oil is a major barrier to its use as a heating oil or for upgrading to other fuels. A total acid number of less than 0.5 mg KOH/g sample is considered acceptable for oils and diesels including biodiesel (ASTM D 6751); this indicates that the acidity of the pyrolysis oil is significantly above acceptable levels and requires treatment for upgrading to a useful product.

6.12: Properties of Oil from Pyrolysis of Sawdust

Temperature (°C)	Total Acid Number Fraction 2 (mg KOH/g of sample)	Total Acid Number Fraction 1 (mg KOH/g of sample)
400	146.6	146.6
475	117.4	100.3
550	61.9	28.2

error 15%

6.13: Total Acid Number of Pyrolysis Oils

	Temperature (°C)	Total Acid Number Fraction 2 (mg KOH/g of sample)	Total Acid Number Fraction 1 (mg KOH/g of sample)
Wheat Straw	400	109.3	109.4
	475	92.3	85.7
	550	47.1	41.9
Poultry Litter	400	69.8	57.3
	475	61.9	49.2
	550	38.3	29.9
Flax Shive	400	100.8	126.7
	475	93.8	85.1
	550	18.8	32.2

error = 15%

6.2.1.3 Density and Viscosity

The density of the pyrolysis oils was not significantly affected by temperature. The oil densities reported in **Tables 6.14 and 6.15** are lower than the value of 1.2 g/cm^3 typically expected (PyNe, 2011). The viscosity of the heavy organic oil fraction is significantly high, similar to the predictions of Mohan et al. (2006) and Pyne (2011), with the observed values being affected by the separation method of the two fractions. The very high viscosities observed here for Fraction 2 are in agreement with those reported by Mullen et al. (2010), which varied from 20 to 1100 mPa·s (cP) at 40°C , depending on the feedstock. The viscosities of the heavy organic Fraction 2 were affected by feedstock type, with those of both straws and poultry being greater than that of the baseline sawdust. Viscosities are normally reduced in bio-oils with higher water content, as demonstrated by the results for Fraction 1, and less water-insoluble components (Zhang et al., 2007), where the composition of the oil has the most significant impact.

6.14: Physical Properties of Oil from Pyrolysis of Sawdust

Temperature ($^\circ\text{C}$)	Density @ 20°C Fraction 2 (g/cm^3)	Density @ 20°C Fraction 1 (g/cm^3)	Viscosity @ 40°C (mPa·s), Fraction 2	Viscosity @ 40°C (mPa·s), Fraction 1
400	0.72	0.72	24 (single fraction oil)	24 (single fraction oil)
475	1.156	1.06	43	16.9
550	1.099	0.534	63	7.8

error 8.1%

6.15: Density and Viscosity of Pyrolysis Oils

	Temperature ($^\circ\text{C}$)	Density @ 20°C Fraction 2 (g/cm^3)	Density @ 20°C Fraction 1 (g/cm^3)	Viscosity @ 40°C (mPa·s), Fraction 2	Viscosity @ 40°C (mPa·s), Fraction 1
Wheat Straw	400	1.157	0.981	-	1.5
	475	1.033	1.013	147	1.4
	550	1.024	1.003	133	1.5
Poultry Litter	400	0.9	0.615	418	2.4
	475	1.076	0.83	-*	8.2
	550	1.114	0.675	-*	5.4
Flax Shive	400	0.923	0.99	130	8.2
	475	1.05	0.6	173	11.0
	550	1.142	1.03	323	6.8

error 8.1%

*Not identified due to solid content or thickness of the sample where viscosity exceeded limit of viscometer.

6.2.1.4 Heating Value

The heating values of the various bio-oils are provided in **Tables 6.16 and 6.17**. In the case of the sample at 400°C, and the Fraction 1 oils, incomplete combustion is responsible for the low heating value due to the high water content in the single-fraction oil. Agblevor et al. (2010) found that poultry litter bio-oils have much higher calorific value (26–29 MJ/kg) than the corresponding hardwood bio-oil (20–22 MJ/kg), a result confirmed in the present SRC study. They concluded that the higher calorific value of the poultry litter bio-oil appears to correlate directly with the protein content of the raw litter. The heating values reported in **Table 6.17** for poultry litter agree with Schnitzer et al. (2007a), as do the minimal heating values of the separated aqueous Fraction 1 of 1 to 4 MJ/kg that were observed. It is noted that all aqueous fractions did not fully combust during bomb calorimetry. Therefore, the heating values of the separated aqueous fractions are not reliable. The lack of combustion of the aqueous fractions is due to their high moisture content. This was also observed by Naik et al. (2009) in the literature.

The heating values for all Fraction 2 oils for all feedstocks are in the expected range reported in Laird et al. (2009), although slightly higher than is typically expected (He et al., 2009; Brown et al., 2010). The heating value is impacted by water content and oxygen content (Oasmaa and Czernik, 1999), as well as pyrolysis temperature. The heating value of the bio-oil was found by He et al. (2009) to increase with decreasing the process temperature. This trend was not observed in this study, likely due to the decreasing water content in the oils with increasing temperature, a factor which improves the combustibility of the oils.

6.16: Properties of Oil from Pyrolysis of Sawdust

Temperature (°C)	Heating Value – Fraction 2 (MJ/kg)	Heating Value – Fraction 1 (MJ/kg)
400	-	0.3*
475	23.9	0.8
550	28.8	2.9

error 2.26

* single fraction oil

6.17: Heating Values of Pyrolysis Oils

	Temperature (°C)	Heating Value – Fraction 2 (MJ/kg)	Heating Value – Fraction 1 (MJ/kg)
Wheat Straw	400	26.8	0.8
	475	22.6	1.8
	550	29.1	0.2
Poultry Litter	400	31.8	0.3
	475	34	0.8
	550	20.5	0.8
Flax Shive	400	27.3	0.8
	475	29.9	1.8
	550	29.9	3.9

error 2.26

6.2.1.5 Elemental Composition

The proximate elemental analysis of the pyrolysis oils is presented in **Tables 6.18 and 6.19**. This agrees with Oasmaa and Czernik (1999) for wood-based oils, although oil oxygen levels frequently make up 35 to 40%. These samples were analyzed after the moisture was removed; therefore, the oxygen and hydrogen contents do not represent the water content, but only bound components. The presence of oxygen creates the primary complicating issue for the difference between pyrolysis oils and hydrocarbon fuels (Zhang et al., 2007). Therefore, pyrolysis oils with lower oxygen content are more desirable for fuel applications, such as from poultry litter. It appears that oil oxygen content decreases with increasing pyrolysis temperature. The primary component of all oils is carbon, as expected due to their biomass feedstocks, with minimal nitrogen and sulphur. The relatively high nitrogen content of poultry litter char compared to hardwood bio-oils (Agblevor et al., 2010) should be investigated, as it may have negative effects on the environment when used as an energy source.

6.18: Proximate Analysis of Bio-oil from Sawdust

Temperature (°C)	% dry basis				
	C	H	N	S	O
400	63.5	6.6	0.8	0.00	29.2
475	66.2	6.0	0.4	0.03	27.3
550	68.8	6.4	0.6	0.2	23.9

6.19: Elemental Composition of Pyrolysis Oils

	Temperature (°C)	% dry basis				
		C	H	N	S	O
Wheat Straw	400	36.2	13.3	0.4	0.01	50.0
	475	45.8	13.0	0.4	0.01	40.8
	550	58.6	10.8	1.2	0.03	29.4
Poultry Litter	400	70.3	10.2	7.0	0.4	12.1
	475	68.4	8.8	8.6	0.1	14.0
	550	65.3	10.5	9.9	0.3	13.9
Flax Shive	400	69.5	7.2	2.0	0.1	21.3
	475	71.4	7.4	2.5	0.0	18.7
	550	75.1	6.8	3.1	0.1	14.9

error 1%

6.2.1.6 Composition by Functional Group

There are 300 chemical compounds that have been identified in bio-oils (Zhang et al., 2007; Schnitzer et al., 2007b), with over 400 present (Marsman et al., 2007), although many present only in very small amounts. The complexity and variation of bio-oils create a major challenge in identification. The composition of the oil according to functional groups was analyzed and is presented in **Tables 6.20 and 6.21**. The total percentage of compounds (wt%) that could be identified and classed by functional group is provided in the last column of these tables. As there were a large number of compounds that were not identifiable by GC-MS, these results provide only a partial indication of the oil composition. This is particularly true of the heavier organic Fraction 2, which means that there are many compounds left unclassified in the results. The range of components and functional groups observed agrees with those reported in the literature (Marsman et al., 2007; Huber et al., 2006). Some compounds were specifically identified within these functional groups. A detailed list of all compounds identified in each oil is attached in the Appendices.

A significant difference in composition was observed between feedstocks and pyrolysis temperatures, as shown in Tables 6.20 and 6.21. The effect of temperature has been reported in the literature by Elliot (1986), who described a relationship between the types of compounds in the products and the temperature to which the vapours were exposed before quenching. Elliot stated that at 400°C, mixed oxygenates were favoured. At 500°C phenolic esters were produced, and at 600°C alkyl phenolics were favoured, corresponding to the high phenolic content of the oils produced in this study for the given temperature range of 400°C

to 550°C. At higher temperatures heterocyclic ethers and polycyclic polyaromatic hydrocarbons are produced.

The phenol content was high in all oils, with the highest content present in the flax shive oils. A high proportion of phenolic compounds are expected in bio-oils made from high-lignin feedstocks such as wheat and flax as (Mohan et al., 2006). As well, phenolic compounds are expected in any biomass-based oil as they include syringols and guaiacols, recognizable as the major components of wood smoke and food smoking, with syringol providing the smoky aroma and guaiacol responsible for smoky taste. Specific phenolic compounds identified include a large variety of oxygenated phenols (wheat straw, poultry litter, flax shive); ethylbenzene (poultry litter), a precursor to polystyrene; and naphthalene- and benzene-derived compounds (poultry litter, flax shive).

Table 6.20: Composition of Baseline Sawdust Oil by Functional Group

Temp. (°C)		Phenols (wt%)	Ketones (wt%)	Alcohols (wt%)	Acids (wt%)	Aldehydes (wt%)	Nitrogen Compounds (wt%)	Other Compounds (wt%)	Identified Compounds (wt%)
400	Fraction 2	-	-	-	-	-	-	-	-
	Fraction 1	27.2*	14.8*	3.2*	0.7*	0*	0*	0*	46.9*
475	Fraction 2	11.3	6.1	3.5	0.6	5.6	0	3.9	31
	Fraction 1	55.3	1.8	3.5	0	0	0	2.7	63.4
550	Fraction 2	29.3	0	2.7	0	0	0	12.4	44.4
	Fraction 1	45.9	0.6	1	0	0	0	0	47.5

*single fraction oil

6.21: Composition of Pyrolysis Oils by Functional Group

	Temperature (°C)		Phenols (wt%)	Ketones (wt%)	Alcohols (wt%)	Acids (wt%)	Aldehydes (wt%)	Nitrogen Compounds (wt%)	Other Compounds (wt%)	Identified Compounds (wt%)
Wheat Straw	400	Fraction 2	38.6	11	0	0	4.7	0	0	54.3
		Fraction 1	18	29.1	8.8	8.4	2	0	0	66.3
	475	Fraction 2	23.5	7.8	5.9	0	12.1	0	0	49.3
		Fraction 1	11	20.7	6.9	23.6	1	0	0	63.2
	550	Fraction 2	13	1.2	0	2.8	5.5	0	0	22.5
		Fraction 1	16.1	10.6	9.8	25.4	0	0	0	61.9
Poultry Litter	400	Fraction 2	17.9	0	6.2	0	0	35.8	0	60
		Fraction 1	23.9	4.6	8.3	0	0	11	3.2	50.9
	475	Fraction 2	12.5	0	6.7	3	0	12.2	0	33.4
		Fraction 1	4.3	16	12.1	0	0	14.9	0.9	48.1
	550	Fraction 2	14.7	0	4.5	3.7	0	13.6	0	36.6
		Fraction 1	10.2	0	10.3	0	0	14.8	3.6	39
Flax Shive	400	Fraction 2	52.4	0.9	2	1.7	0	0	0	57
		Fraction 1	36	0	5.8	0	0	0	6.4	48.1
	475	Fraction 2	47.1	5.6	2.1	0	0	0	6.5	61.2
		Fraction 1	26.9	0	3.2	0	0	0	3.5	33.6
	550	Fraction 2	62.6	9.9	3.3	0	0	0	1.45	77.2
		Fraction 1	29.3	0	10.8	0	0	0	0	40

The presence of ketones was observed to be significant in wheat, but low in other feedstocks, including the baseline. The ketone content tends to decrease with temperature, except in flax where the opposite effect was observed. The esters, acids, alcohols, ketones, and aldehydes are believed to form from decomposition of the miscellaneous oxygenates, sugars (aldehydes), and furans (ethers), which form from cellulose and hemicellulose (Huber et al., 2006). Furans are an aromatic heterocyclic compounds and are considered to be possibly carcinogenic (U.S. Department of Health and Human Services, 2001). These were not identified specifically in this study. Specific ketone compounds identified in the oils in this study included: ethanones (wheat straw), furanones (wheat straw), flammable hydrocarbons such as cycloalkanes (wheat straw) and cycloalkenes (poultry litter, flax shive). Mohan et al. (2006) showed that cellulose produces anhydrocellulose and levoglucosan, indicating that they should be present in all oils produced in this study. Levoglucosan is a dehydrated glucose with a ketone functional group, but was not isolated specifically.

Alcohols were present in all oils, with the highest measured in poultry litter oils. Specific compounds identified included: furfuryl alcohols used in making sealants, cements, and resins (wheat straw), mequinol used in depigmentation drugs (poultry litter), and benzene diols (poultry litter, flax shive).

Acids were highest in the wheat straw oils, with low or negligible amounts identified in the other oils. This result would appear to contradict the high acidity of all of the pyrolysis oils (Table 6.13), especially as hemicellulose containing biomass was found to yield significant amounts of acetic acid (Mohan et al., 2007). However, many acid compounds, including acetic acid, were not classified due to the limitations of the GC-MS technique and the complex composition. As well, many phenolic compounds contribute significantly to the acidity of an oil. Specific compounds identified in this study included: propanoic acids (wheat straw), other cycloalkane derivatives (wheat straw, poultry litter), benzoic acids (flax shive), and phosphonic acid (poultry litter) known to be effective as chelating agents and in the inhibition of scale formation in industrial applications.

Identifiable aldehydes were highest in the wheat straw oils, with negligible amounts identified in the other oils. Specific compounds identified included benzaldehydes (wheat straw).

Nitrogen compounds were significant only in the poultry litter oils. The presence of nitrogen compounds in these oils can be explained by the presence of feces and its higher nitrogen

content. The same phenomenon was observed in char produced from poultry litter. The specific compounds identified in poultry litter included: pyridines, pyrazoles, indoles, and cycloalkanes. Pyridines are precursors to a variety of agrochemicals and pharmaceuticals.

Other unclassified compounds were also observed in the oils, these included primarily alkane (hydrocarbon) compounds. A significant portion of the unidentified compounds present in each oil are likely made up of suspended solids and pyrolytic lignin (Dynamotive, 2011).

6.2.2 Char

Characterization was carried out to evaluate possible applications for biochar use. The properties and composition of the chars are presented here relative to the type of feedstock and temperature.

6.2.2.1 Moisture and Ash Content

The moisture contents shown in **Tables 6.22 and 6.23** of the biochar were all less than 10%, as is desirable. For the straws, the moisture content increased with temperature, whereas the opposite effect was observed for the baseline sawdust and the poultry litter. For all feedstocks, the ash content increased with temperature, with the highest contents being observed for poultry due to the higher ash content in the poultry litter feedstock. In Agblevor et al. (2010) the biochar ash content of the biochar ranged from 24 to 54 wt% and was very rich in inorganic components such as potassium and phosphorous. This shows evidence that the ash content of the sample is directly related to char formation.

6.22: Properties of Pyrolysis Char from Sawdust

Temperature (°C)	Moisture (wt %)	Ash (% d.b.)
400	3.01	1.82
475	4.02	3.13
550	7.85	3.99

error = 0.7

error = 1.7

6.23: Moisture Content of Pyrolysis Chars

	Temperature (°C)	Moisture (wt %)	Ash (% d.b.)
Wheat Straw	400	1.97	5.2
	475	6.2	7.35
	550	6.31	8.28
Poultry Litter	400	2.31	33.28
	475	1.16	40.5
	550	1.7	46.31
Flax Shive	400	8.3	8.93
	475	3.51	9.36
	550	5.67	10.64

error = 0.7

error = 1.7

6.2.2.2 Ultimate Analysis

The ultimate analyses (dry basis) of the produced chars are given in **Tables 6.24 and 6.25**. Char from poultry litter had more sulphur than that from the straws and sawdust. This is due to the presence of feces in the feedstock. The low sulphur content of biochar is considered suitable for industrial combustion as this low content does not require technology for removing sulphur oxides from emissions (Laird et al., 2009). As temperature increases, the oxygen and hydrogen content decreases, which corresponds to the findings of Bruun et al. (2011). A minimum of 20% carbon in biochar is expected for all biochars (International Biochar Initiative, 2009), as well as an H/C ratio of less than 0.6.

6.24: Ultimate Analysis of Char from Sawdust

Temperature (°C)	C	H	N	S	O
400	71.50%	4.72%	0.05%	0.02%	23.56%
475	80.39%	3.81%	0.14%	0.00%	15.66%
550	81.32%	3.57%	0.17%	0.01%	14.92%

6.25: Ultimate Analysis of Pyrolysis Chars

	Temperature (°C)	C	H	N	S	O
Wheat Straw	400	71.3%	4.9%	0.6%	0.6%	22.7%
	475	74.9%	3.9%	0.6%	0.1%	20.5%
	550	83.1%	3.2%	0.6%	0.2%	12.9%
Poultry Litter	400	73.1%	6.2%	10.5%	1.7%	8.6%
	475	77.1%	4.7%	9.1%	2.8%	6.3%
	550	83.0%	4.2%	8.4%	2.9%	1.5%
Flax Shive	400	71.2%	5.0%	1.2%	0.1%	22.6%
	475	76.6%	4.4%	1.0%	0.00%	18.0%
	550	82.6%	3.7%	1.0%	0.02%	12.7%

6.2.2.3 Heating Value

The heating values for all biochars, given in **Tables 6.26 and 6.27**, were higher than reported in the literature (Laird et al., 2009). For the straws, wheat and flax, the heating values increased with increasing pyrolysis temperature. This agrees with Agblevor et al. (2010). Aguiar et al. (2008) also found that an increase of temperature increased char's heating value (about 3000 kJ/kg in this temperature range). No significant effect was observed for the poultry litter in the present project. Any observed changes in heating values were very small when the error in the results is considered.

6.26: Properties of Pyrolysis Char from Sawdust

Temperature (°C)	Heating value (MJ/kg)
400	24.4
475	28.6
550	26

error = 2.05

6.27: Heating Values of Pyrolysis Chars

	Temperature (°C)	Heating value (MJ/kg)
Wheat Straw	400	21.9
	475	25.2
	550	25.8
Poultry Litter	400	23.9
	475	18.9
	550	18.7
Flax Shive	400	21.8
	475	26.3
	550	30.1

error =2.05

6.2.2.4 Particle Size

The particle size distribution is described in **Tables 6.28 and 6.29**. The char particle size tended to decrease with increasing pyrolysis temperature, as observed by Bruun et al. (2011), with particle sizes corresponding to the present data. The reduction in particle char particle size with increased pyrolysis temperature is expected as at higher temperature more compounds are volatilized, and more quickly. Detailed particle size distributions for char are in the Appendices.

6.28: Particle Size Char from Sawdust

Temperature (°C)	Particle Size: Smaller Than 10% of Sample (µm) D(v,0.1)	Particle Size: Smaller Than 50% of Sample (µm) D(v,0.5)	Particle Size: Smaller Than 90% of Sample (µm) D(v,0.9)
400	19	81	290
475	14	66	334
550	29	133	505

6.29: Particle Size Distribution of Pyrolysis Chars

	Temperature (°C)	Particle Size: Smaller Than 10% of Sample (μm) D(v,0.1)	Particle Size: Smaller Than 50% of Sample (μm) D(v,0.5)	Particle Size: Smaller Than 90% of Sample (μm) D(v,0.9)
Wheat Straw	400	10	78	343
	475	5	35	244
	550	6	24	106
Poultry Litter	400	20	96	433
	475	8	38	237
	550	7	38	394
Flax Shive	400	10	71	306
	475	8	40	237
	550	10	49	383

6.2.2.5 Porous Characteristics

Tables 6.30 and 6.31 provide data on the porous characteristics of the biochars. There was no significant difference in pore volume between trials and no observable trend in surface area with temperature. Bruun et al. (2011) observed an increase in porosity with increasing pyrolysis temperature. The surface area was greater for all feedstocks relative to the baseline sawdust, which is explained by the larger particle size of the baseline char. Given the decreasing average particle size with increasing temperature observed in Table 6.29, it would be expected that the surface area would also increase with temperature. This is not the case as observed in Table 6.31, possibly due to the impact of heating time of the surface area (Kwapinski et al., 2010).

6.30: Porous Characteristics of Char from Sawdust

Temperature (°C)	Surface Area (m^2/g)	Total Pore Volume (cm^3/g)
400	2.7	0.003
475	3.3	0.002
550	2.7	0.002

6.31: Porous Characteristics of Pyrolysis Chars

	Temperature (°C)	Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)
Wheat Straw	400	4.2	0.002
	475	3.8	0.002
	550	3.2	0.001
Poultry Litter	400	-	0.001
	475	7.4	0.002
	550	2	0.001
Flax Shive	400	4.5	0.004
	475	2.2	0.001
	550	3.6	0.005

error = 0.2

6.2.2.6 pH

The pH of the produced biochars was measured and these are presented in **Tables 6.32 and 6.33**. The pH of the chars tended to increase with temperature for all feedstocks. All pH values were greater for the trial feedstocks than for the baseline.

6.32: pH Values of Pyrolysis Char from Sawdust

Temperature (°C)	pH
400	4.4
475	4.8
550	5.1

error = 0.1

6.33: pH Values of Pyrolysis Chars

	Temperature (°C)	pH
Wheat Straw	400	7.8
	475	9.5
	550	9.6
Poultry Litter	400	7.8
	475	9.4
	550	9.5
Flax Shive	400	6
	475	7.2
	550	8

error = 0.1

6.2.3 Gas

6.2.3.1 Composition

The composition (mol%) of the pyrolysis off-gas produced are given in **Tables 6.34 and 6.35**. An increase in hydrocarbon and hydrogen content was observed with increasing temperature for all feedstocks in this study, usually with accompanying reduction in carbon dioxide. Aguiar et al. (2007) also found that the yields of hydrogen and methane increased with temperature, concurrent with decreasing carbon monoxide, with an accompanying reduction in carbon dioxide. The high carbon dioxide and carbon monoxide yields, and lower hydrogen and hydrocarbon yields, are as predicted by Dr. Peter Fransham of ABRI-Tech Inc. who reported typical hydrogen at 6% and methane and other hydrocarbons at more than 10%. These results also differ from the work of Ratcliff et al. (2002) in that significantly smaller amounts of methane and hydrogen are present, as well as substantially more carbon dioxide. The major components of pyrolysis gas were carbon dioxide and carbon monoxide with smaller fraction of low molecular weight hydrocarbons in Agblevor et al. (2010), similar to those fractions observed here. The high amounts of carbon dioxide and carbon monoxide observed in this study may be the result of some simple combustion occurring in the process rather than entire pyrolysis of biomass. Improvements to the unit design may be able to mitigate this problem.

6.34: Composition of Pyrolysis Gas from Sawdust

Temp. °C	CO ₂ (%)	CO (%)	H ₂ (%)	Methane (%)	Ethane (%)	Ethylene (%)	Propane (%)	N ₂ (%)	O ₂ (%)	Unidentified (%)
400	48.3	39.2	1.5	2.7	0	0	0	7.5	0	1.0
475	34.6	42.4	5.3	8.0	0.6	0.5	0	3.2	0	5.6
550	24.0	34.2	16.9	12.3	1.4	0.5	0	2.4	0	8.4

6.35: Composition of Pyrolysis Gases

	Temp. °C	CO ₂ (%)	CO (%)	H ₂ (%)	Methane (%)	Ethane (%)	Ethylene (%)	Propane (%)	N ₂ (%)	O ₂ (%)	Unidentified (%)
Wheat Straw	400	52.6	32.7	1.5	2.0	0	0	0	4.4	32.7	6.5
	475	-	-	5.4	4.8	1.8	1.9	1.7	-	7	-
	550	30.6	34.4	9.4	6.3	1.9	1.9	1.5	5.2	34.4	7.6
Poultry Litter	400	68.7	15.9	2.3	1.4	0	0	0	2.6	0	9.3
	475	60.1	19.6	2.8	1.7	0	0	0	2.7	1.4	11.7
	550	37.8	22.1	10.0	5.4	0	0	0	3.7	5.9	15.3
Flax Shive	400	52.6	32.7	1.4	1.9	0	0	0	4.4	0.6	6.4
	475	-	-	5.4	4.8	1.8	1.9	1.7	-	9.0	-
	550	27.4	25.4	15.8	13.5	1.9	1.1	1.1	10.0	0	4.1

6.3 Mass and Energy Balance

The values of mass and energy collected during the pyrolysis trials (Section 6.2.1) were used to determine the mass and energy balance for the pyrolysis unit. The mass and energy balance schematic for pyrolysis of all feedstocks and temperatures is given in **Fig. 6.1**. The mass and energy balance values for each schematic identifier are provided in **Table 6.36**. The density of compressed propane is assumed to be 0.493 kg/L (25°C) and the heating value of propane is 24.7 MJ/L (PGAC, 2005).

The feedstock with the highest heating value is the poultry litter, resulting in higher oil and gas heating values for its products. The calculated heating value of off-gas for all feedstocks increased with temperature, due to increased presence of hydrocarbons and hydrogen in the gas product. Conversely, the heating value of the oils and chars was reduced at the maximum temperature of 550°C. As expected, the energy required to reach the reactor temperature increased with pyrolysis temperature. The pyrolysis of poultry litter requires the most energy input of all feedstocks, due to both its higher biomass feeding rate and higher moisture content. The results of the mass and energy balance were in agreement with Badger and Fransham (2006) for a system of similar design. The error in this balance is associated with the neglected product losses in closing the mass balance for the gas product. These losses can be 10% or more of the total mass.

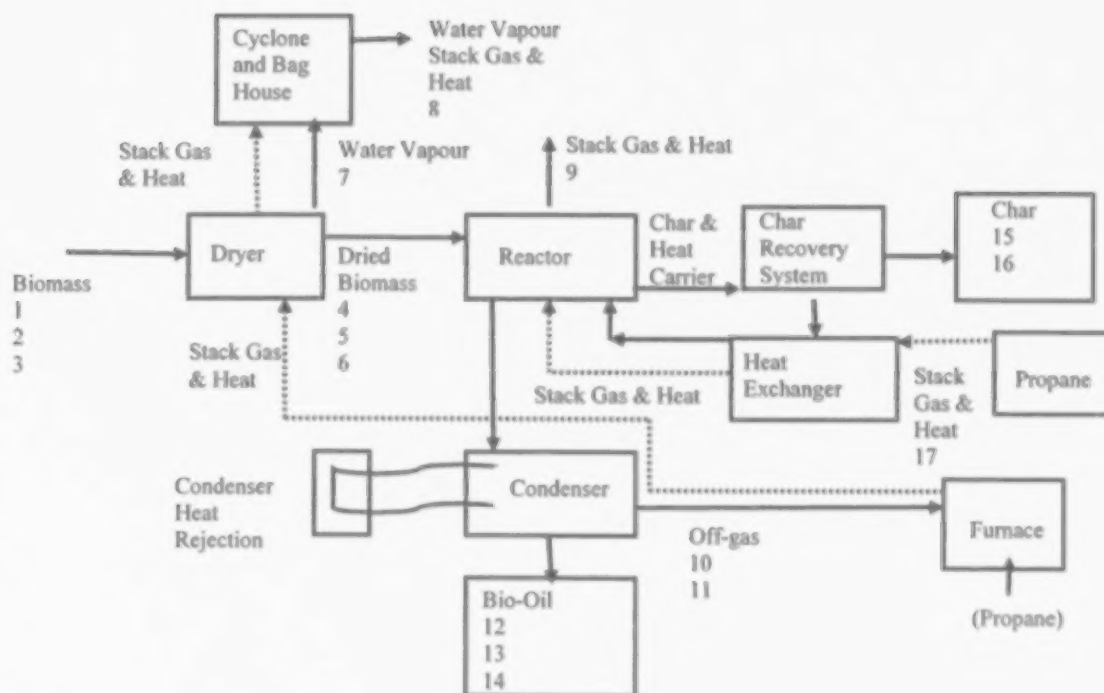


Fig. 6.1: Mass and energy balance for pyrolysis unit for poultry litter at 400°C (hourly operation).

6.36: Results of Mass and Energy Balance for All Feedstocks and Pyrolysis Temperatures

Feedstock	Baseline	Baseline	Baseline	Wheat Straw	Wheat Straw	Wheat Straw	
Pyrolysis Temperature (°C)	400	475	550	400	475	550	
Figure Identifier							Units
Biomass							
1	18	18	18	15	15	15	kg/h
2	15	15	15	15	15	15	% moisture
3	359	359	359	299	221	221	MJ/h
Dried Biomass							
4	17	17	17	14	14	14	kg/h
5	6	6	6	6	6	6	% moisture
6	328	326	224	292	203	152	MJ/h
Water Vapour							
7	2	2	2	1	1	1	kg/h
Stack Gas & Heat, Water Vapour							
8	31	33	135	7	18	69	MJ/h
Stack Gas & Heat							
9	250	165	345	106	57	189	MJ/h
Off-gas							
10	8	4	11	2	3	7	kg/h
11	30	32	134	7	18	69	MJ/h
Oil							
12	6	10	4	7	6	2	kg/h
13	6	9	4	7	6	2	L/h
14	152	228	106	187	139	64	MJ/h
Char							
15	3	3	2	5	5	4	kg/h
16	61	81	48	105	124	113	MJ/h
Stack Gas & Heat							
17	105	115	140	100	100	145	MJ/h

Feedstock	Poultry Litter	Poultry Litter	Poultry Litter	Flax Shive	Flax Shive	Flax Shive	
Pyrolysis Temperature (°C)	400	475	550	400	475	550	
Figure Identifier							Units
Biomass							
1	26	26	26	13	13	13	kg/h
2	30	30	30	15	15	15	% moisture
3	604	604	604	221	221	189	MJ/h
Dried Biomass							
4	20	20	20	12	12	12	kg/h
5	10	10	10	8	8	8	% moisture
6	596	590	574	210	191	139	MJ/h
Water Vapour							
7	6	6	6	1	1	1	kg/h
Stack Gas & Heat, Water Vapour							
8	8	14	30	11	30	50	MJ/h
Stack Gas & Heat							
9	236	313	475	130	138	110	MJ/h
Off-gas							
10	3	5	5	3	4	4	kg/h
11	5	11	27	11	30	49	MJ/h
Oil							
12	11	9	10	6	4	5	kg/h
13	10	9	10	6	4	5	L/h
14	336	297	208	159	128	160	MJ/h
Char							
15	7	7	5	3	3	2	kg/h
16	160	127	99	62	85	68	MJ/h
Stack Gas & Heat							
17	130	135	180	130	130	150	MJ/h

7. ASSESSMENT OF APPLICABILITY OF PYROLYSIS FOR SPECIFIC END-USES

7.1 Oil

Bio-oils can be used as combustion fuels and for power generation, making those with high heating values (such as straw oils at higher temperatures, or poultry litter at lower temperatures) superior for this purpose. Bio-oil can also be gasified for the production of syngas rather than combusted as a fuel.

Oils can also be used for production of specialty chemicals; the suitability for this, of course, depends on the composition of the bio-oil and the desired chemical. For example, ethylbenzene is present in significant quantities in oils from poultry litter, and it is a precursor to polystyrene, used in plastic products. Phenols, found in all oils studied here, are used in a variety of resins. Mequinol used in depigmentation drugs is also found in oils from poultry litter, as is phosphonic acid known to be an effective chelating agent and used in the inhibition of scale formation in industrial applications. Pyridines are precursors to a variety of agrochemicals and pharmaceuticals, including anti-bacterial and anti-viral drugs, antihistamines, water repellents, bactericides, and herbicides. They are also used as a solvent and reagent in many processes. Furfuryl alcohols, found in wheat straw derived oils, are used in making sealants, cements, and resins. A further example is production of anhydro-sugars like levoglucosan from high cellulose feedstocks such as the agricultural residues studied in this project. The hydrolysis of levoglucosan generates the fermentable sugar glucose, and therefore lignocellulosic material exhibits great potential as a renewable feedstock for the production of biofuels.

Although bio-oil is not suitable as a transportation fuel, it can be upgraded to such fuel. The oils most suitable to upgrading are those with reduced oxygen content, water content, and acidity. The pyrolysis oil with the lowest water content in this study was poultry litter oil produced at the highest temperature of 550°C, as content decreases with temperature, although that of the baseline sawdust was even lower. The lowest oxygen content was also observed in the poultry litter, making it seem superior to the other oils for upgrading. As well, the lowest acidity was observed in the poultry litter oil at 550°C. Pyrolysis oil could also be used as an energy densification medium to improve the economics of biomass transportation and storage.

7.2 Char

The high heating value of all the biochars studied in this project makes them suitable for use as a combustible fuel. The highest heating values observed in the study were for flax shive at 550°C, as the heating value tends to increase with temperature. Most biochars used as soil amendments are ideally neutral to slightly basic in pH, making the baseline biochar too acidic for most soil applications. However, with pH adjusted using different additives, the biochars produced in this study could still be used as soil amendments. The char from wheat straw at 550°C provided the most basic biochar, ideal for acidic or degraded soils. Chars can also be activated by steam or microbes and used in filtering and bioremediation.

7.3 Gas

The composition of the gases produced in this study was very high in carbon dioxide and carbon monoxide. The content of hydrogen and hydrocarbons was low, making it a very poor syngas. Pyrolysis gas containing significant amounts of carbon dioxide along with methane can be used as a fuel for industrial combustion purposes, although the low proportion of methane observed here may reduce the value of the gas for this application. Pyrolysis gas can also be upgraded to fuels; however, the low hydrogen and hydrocarbon content observed in this study may make further upgrading challenging. The pyrolysis gas produced is presently being burned successfully to operate the dryer attached to the unit, and this use could be extended to heating the reactor itself and reducing propane use significantly. The low hydrogen and hydrocarbon production may be a result of the pyrolysis unit design, which continues to be improved. The baseline feedstock of hardwood sawdust had the greatest hydrogen and hydrocarbon contents, increasing with temperature to 550°C, with poultry litter having the highest carbon dioxide content.

8. CONFIRMATION OF BUSINESS CASE FOR COMMERCIALIZATION

8.1 Economics

The capital cost of the pyrolysis unit itself is \$160,000. (Note: all costs and prices are cited in Canadian dollars.) The delivered biomass feedstock price is assumed to be \$20 per metric tonne, although actual feedstock prices range from \$0 to \$83 (Brown et al., 2010). Propane is valued at \$0.80/L (NRCan, 2011), and electricity at \$0.10/ kWh (SaskPower, 2011). Bio-oil, having 50% the heating value of heating oil #2, is valued at 50% of the value of heating oil at \$1.50/L (NRCan, 2011). It is assumed that biochar is valued as biofertilizer at 50% of the value of commercial fertilizers, presently at \$0.60/kg (Drovers Cattle Network, 2011). The value of carbon offset of biochar is assumed to be \$20 per metric tonne in the year 2015 (Brown et al., 2010). With the values described above, and the total mass and energy flows as described in Figure 6.1, the payback period of the project would be 8.7 years with an internal rate of return (IRR) of 2.6%. The results of economic analysis are provided in the Appendices. This assumes a biochar and carbon offset value that is presently theoretical. The economic picture is also affected by the inability to reach the throughput capacity of the pyrolysis unit as received by the manufacturer.

The economic assessment is extremely sensitive to the value of the pyrolysis products. An increase in \$0.10 in the value of bio-oil reduces the payback period to 7.0 years and increases the IRR to 7.1%. An increase in char value by \$0.10 also improves the economics, but to a lesser degree. The carbon offset must be increased from \$20 per tonne to \$180 per tonne to observe the same degree of effect as that of bio-oil price.

The economic assessment of the mobile pyrolysis unit technology may be improved in the future by the following:

- If gasoline is refined from the bio-oil, provided a practical and inexpensive method is used, it provides revenues of \$1.28/L gasoline equivalent. This value will increase as the price of gasoline and oil increases in the coming years. This will also increase the replacement value of pyrolysis gas over propane for heating.
- New uses, chemical products, and upgrading techniques for oil may increase its value.
- With projected implementation and increases in carbon offset the economics improve substantially.

- A strong market for biochar as a soil amendment/fertilizer would increase the value of that product.
- Improvements to the pyrolysis unit design, which impact capacity, product distribution, and product value for various end-uses.

The detailed economic evaluation is presented in the Appendices.

8.2 Business Value

There are other considerations beside the direct economics to the value of the project. The mobile approach to pyrolysis sidesteps a fundamental economic hurdle in biofuels; transporting biomass is expensive because of its bulk volume, whereas liquid fuel from biomass is far more economical to transport (Venere, 2010).

However, this unit is not ready for commercialization as it is presently designed. The commissioning and pyrolysis trials indicated that significant modifications are required to make it more efficient to operate, more suitable for a variety of feedstocks, and practical for mobile operation. The unit is not truly mobile and self-sufficient, requiring electrical power for monitoring and operation. It also requires minimum of two people to operate, with four being preferable, and all must be trained carefully due to safety concerns, causing problems with an ever-changing locale of operation. As well, new feedstocks require significant work on pre-processing and trial and error to develop an operational protocol. This technology, however, bears further investigation and technical development, as it provides an avenue for agricultural residue management, for carbon sequestration, and for distributed energy generation in remote areas.

9. CONCLUSIONS AND RECOMMENDATIONS

The operation, products, and economics of a novel mobile pyrolysis technology were assessed to determine its mobility, robustness, and efficiency for utilization of various agricultural feedstocks, specifically wheat straw, poultry litter, and flax shives. This was done through the characterization of products and their potential value in combination with an assessment of the capital cost and operating costs for the selected pyrolysis technology.

Pyrolysis products are feedstock dependent as well as highly dependent on the technology and the operating conditions. Pyrolysis oil and char were characterized in such a way that their value in various end-uses could be assessed. The impact of temperature and feedstock on product properties was observed in this study. These are summarized as follows:

- For oil used as a combustion fuel, straw-based oils have the highest heating values.
- The superior pyrolysis oil for upgrading seems to be that produced from poultry litter at 550°C, due to its low oxygen content and acidity.
- The best chars for use as a fuel are those from flax shive at 550°C, with all being suitable as soil amendments based on composition, pH, and physical characteristics.
- The interactions that exist between technology, feedstocks, and operating conditions must still be further optimized in order to develop the operating procedures and instructions for yielding a product with consistent characteristics.

At present, the economics of the pyrolysis technology are not favourable, with a payback period of 8.7 years and IRR of 2.6%, and this only with an assumed carbon offset value of the biochar. The economics can be improved by:

- Cost increase for fuels and energy derived from fossil fuels
- Implementation and increase in carbon offset values for products
- Development of an inexpensive and practical method of oil upgrading
- Market development for char as a biofertilizer
- Improvement in unit design to increase capacity and yields of high value products

The amount of agricultural residues within Saskatchewan is extensive and the value of them has significant opportunity for growth. The economics may also be improved by increased energy prices in the future.

The pyrolysis unit itself, as assessed, has promising potential but requires additional modification and upgrading to be made commercially viable. Recommendations are as follows:

- The mobile pyrolysis unit requires redesign work away from the involvement of the manufacturer, to improve oil production and char separation, as well as consistency of operation. The unit requires additional work to make it truly mobile and able to operate fully as a standalone unit in the field. If it can be made so, then this mobility becomes a significant asset to the technology.
- The unit operation requires simplification, so that it no longer requires a minimum of two people, preferably four, working at all times to operate it; the current labour and skill requirements make it impractical for use in a series of remote farm settings.

This research expanded SRC's capabilities and provided a venue for pilot demonstration of mobile pyrolysis technology. This project has highlighted the value and potential of pyrolysis technology, and may allow SRC and the Province of Saskatchewan to support other similar technologies within the province.

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APPENDICES

A. Pyrolysis Unit Specifications

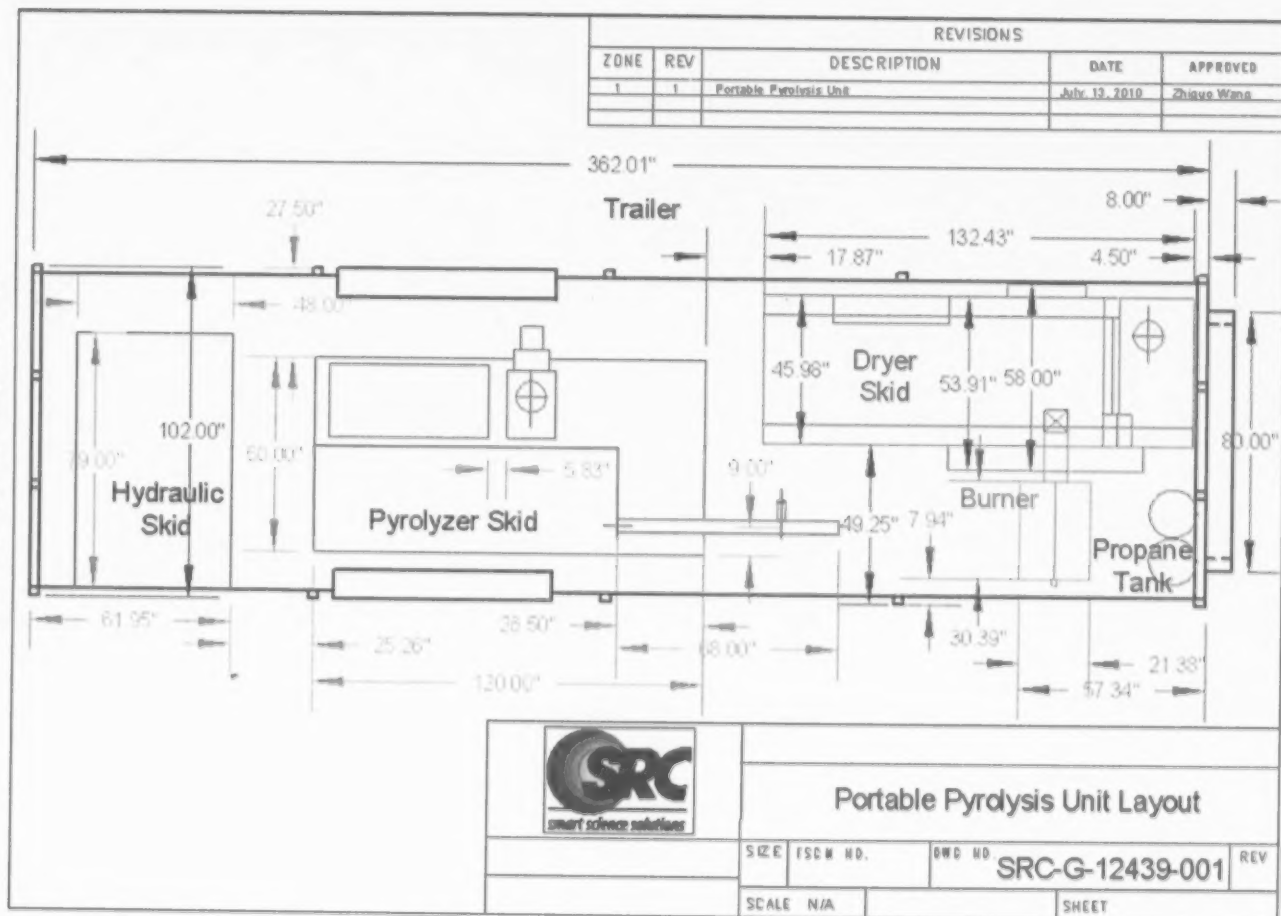


Fig. A1: Schematic of Pyrolysis Unit.

Fig. A2: Flowsheet of Dryer Skid.

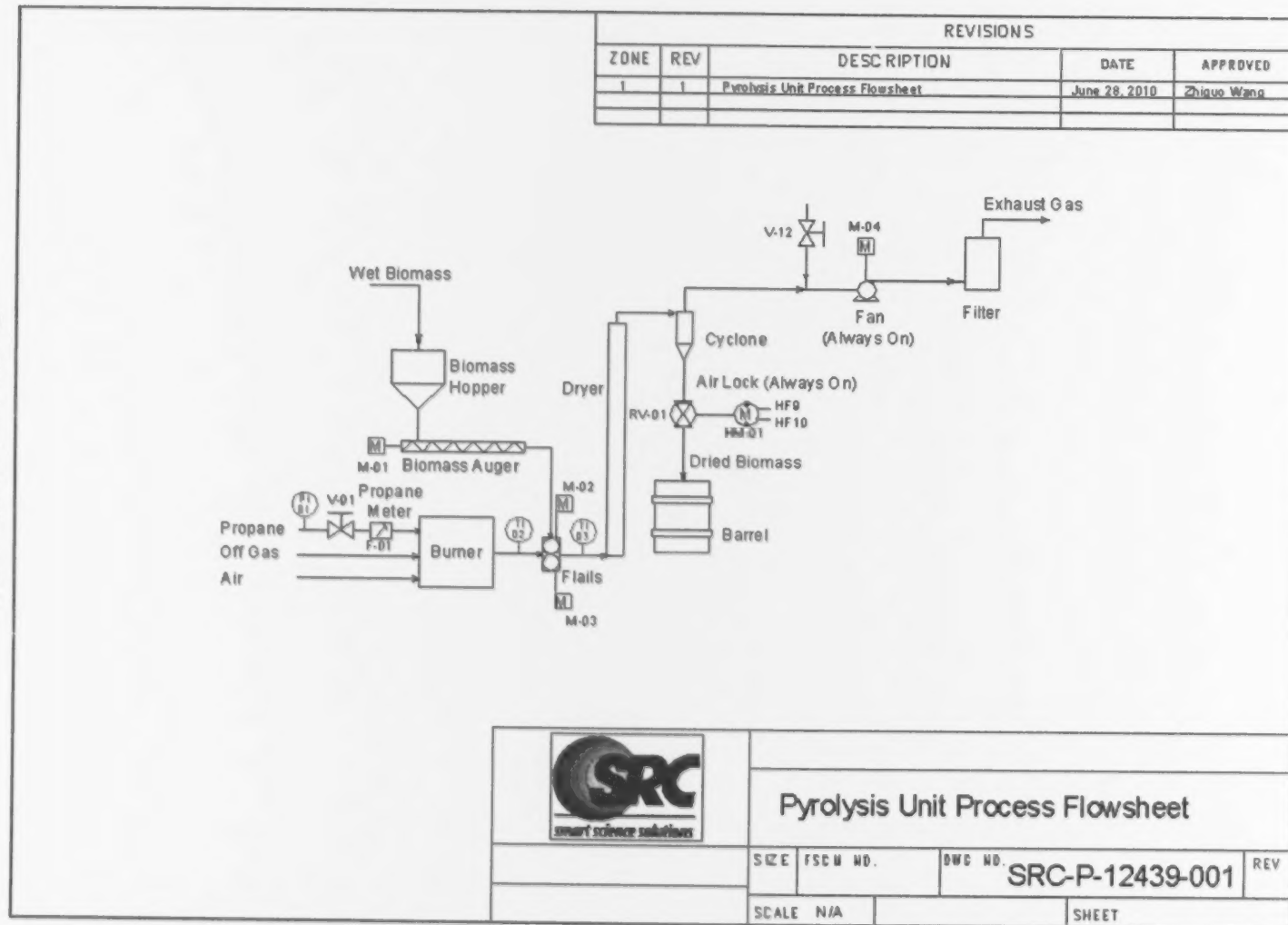


Fig. A3: Flowsheet of Pyrolysis Skid.

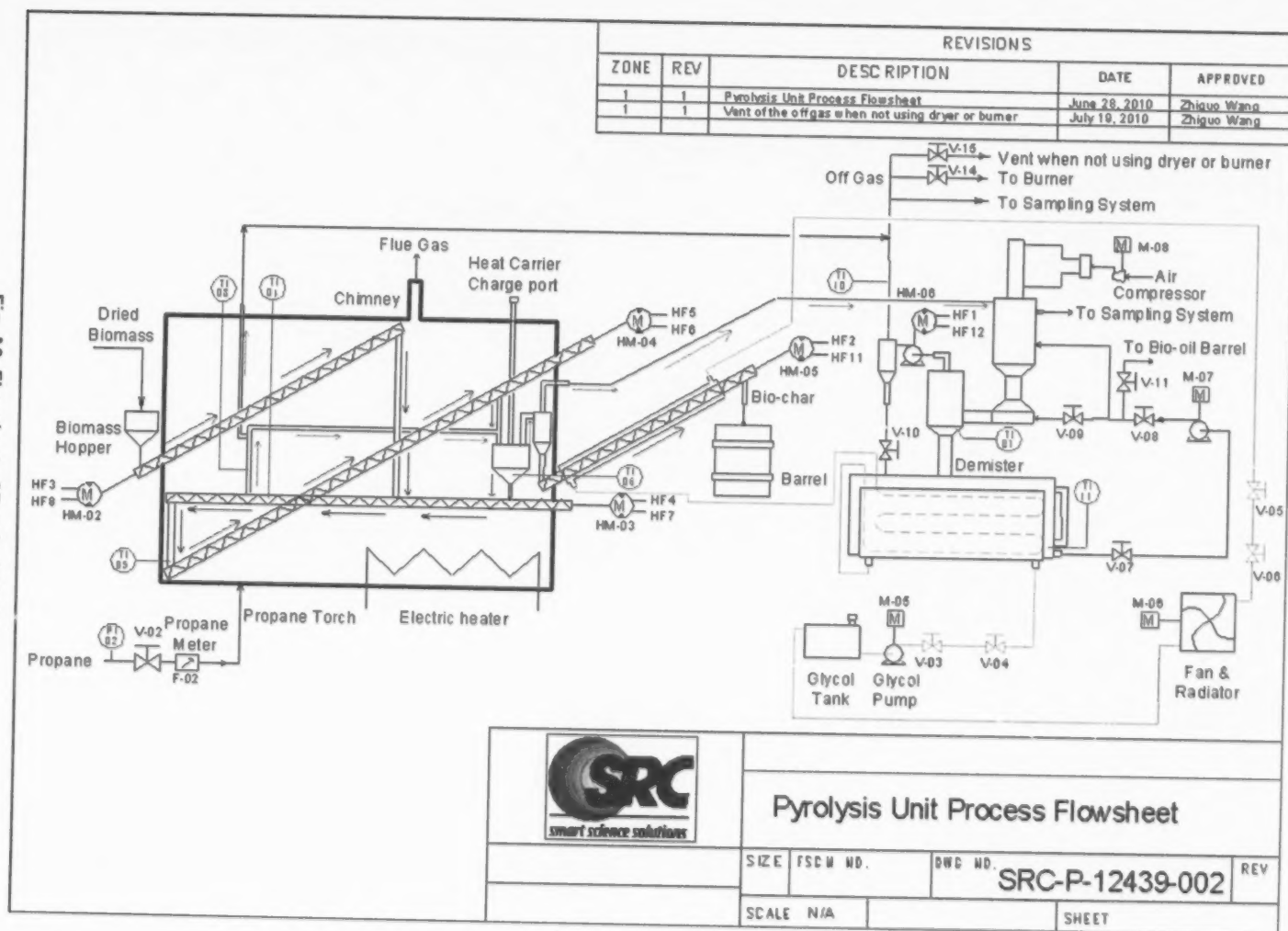
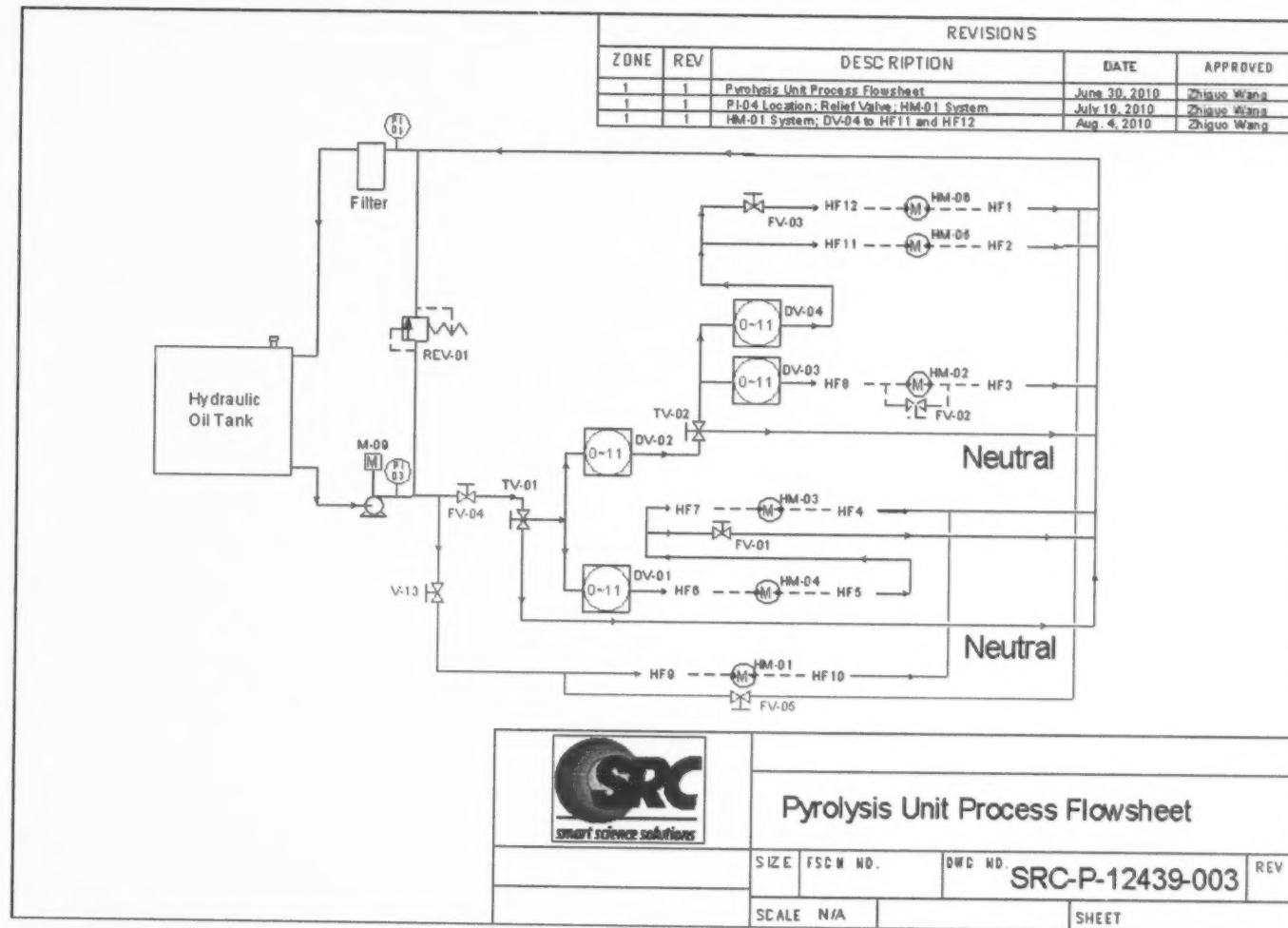


Fig. A.4: Flowsheet of Hydraulic Skid.



B. Photos of Pyrolysis Unit in Operation

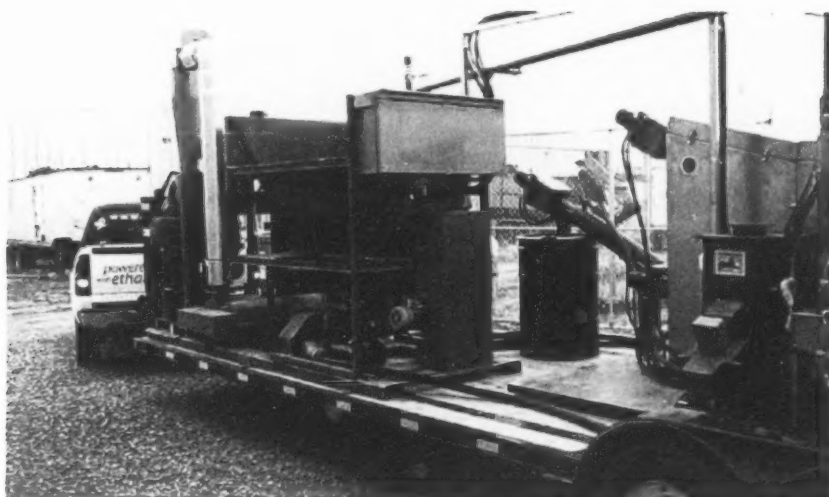


Fig. B.1: Transportation of Pyrolysis Unit

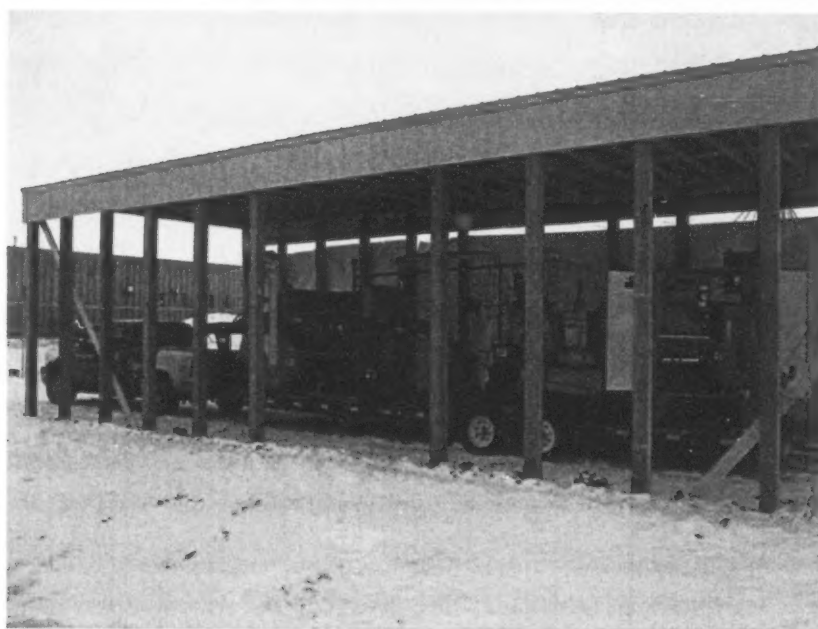


Fig. B.2: Outdoor Operation in SRC Yard

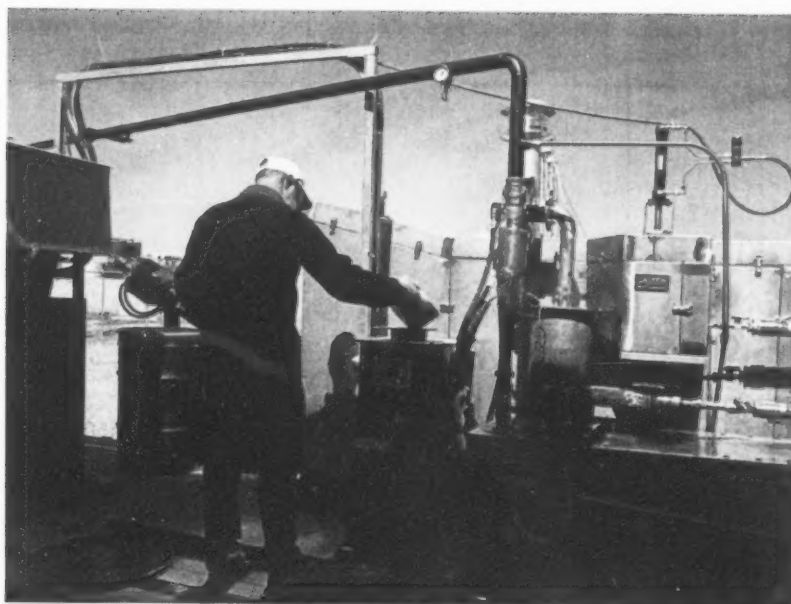


Fig. B.3: Feedstock Loading Trial

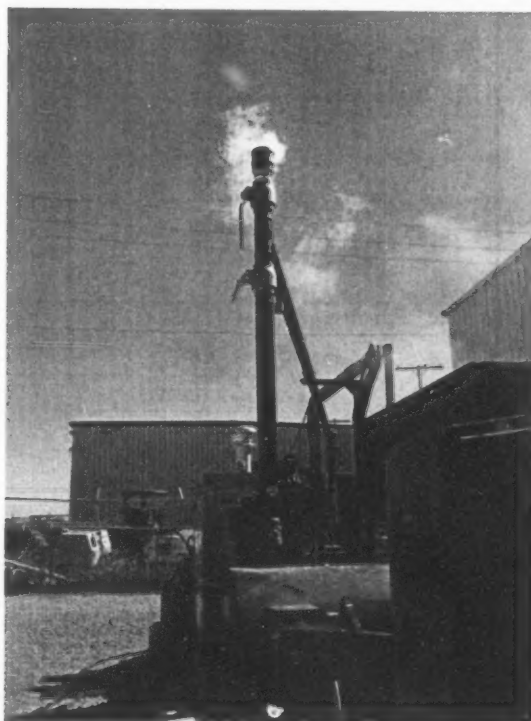


Fig. B.4: Pyrolysis Unit Operation

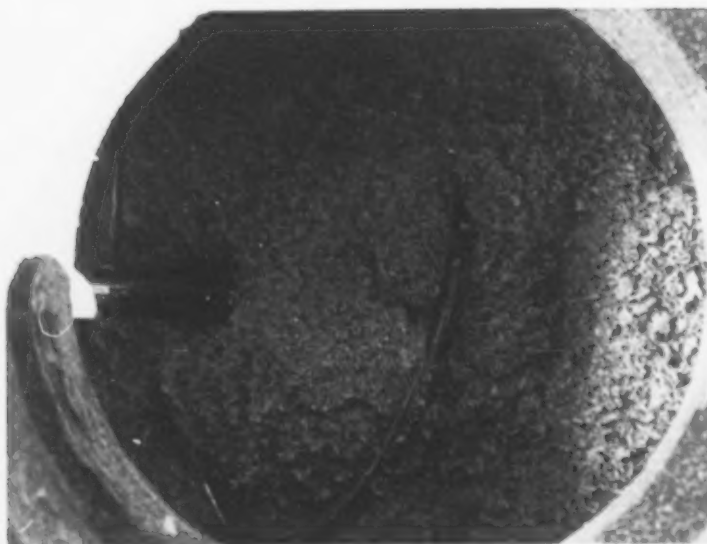


Fig. B.5: Feedstock Loading by Auger

C. Prioritization of Feedstock Selection

C.1: Relative Importance of Feedstock Prioritization Criteria

Project Requirements	Degree of Importance to the Project (1 to 10)	Satisfaction with Current Offering (1 to 10)	Overall Priority (Importance/(Current Offering))	Relative Importance (%)
Low Value of Feedstock	6	5	1.2	9
High Volume of Feedstock Produced	3	5	0.6	4
Disposal Difficulty/Cost of Feedstock	8	5	1.6	12
Environmental Concerns of Feedstock	5	5	1.0	7
Market for Technology if Feedstock Selected	8	5	1.6	12
Fit to Technology	8	5	1.6	12
Feedstock Collection	3	5	0.6	4
Public Perception	4	5	0.8	6
Additional Preprocessing requirements (grinding, drying, special handling, leaching etc.)	8	5	1.2	9
Potential for High-value End-Use - Oil	8	5	1.6	12
Potential for High-value End-Use - Char	8	5	1.6	12

C2: Prioritization Matrix for All Feedstocks under Consideration – Part 1

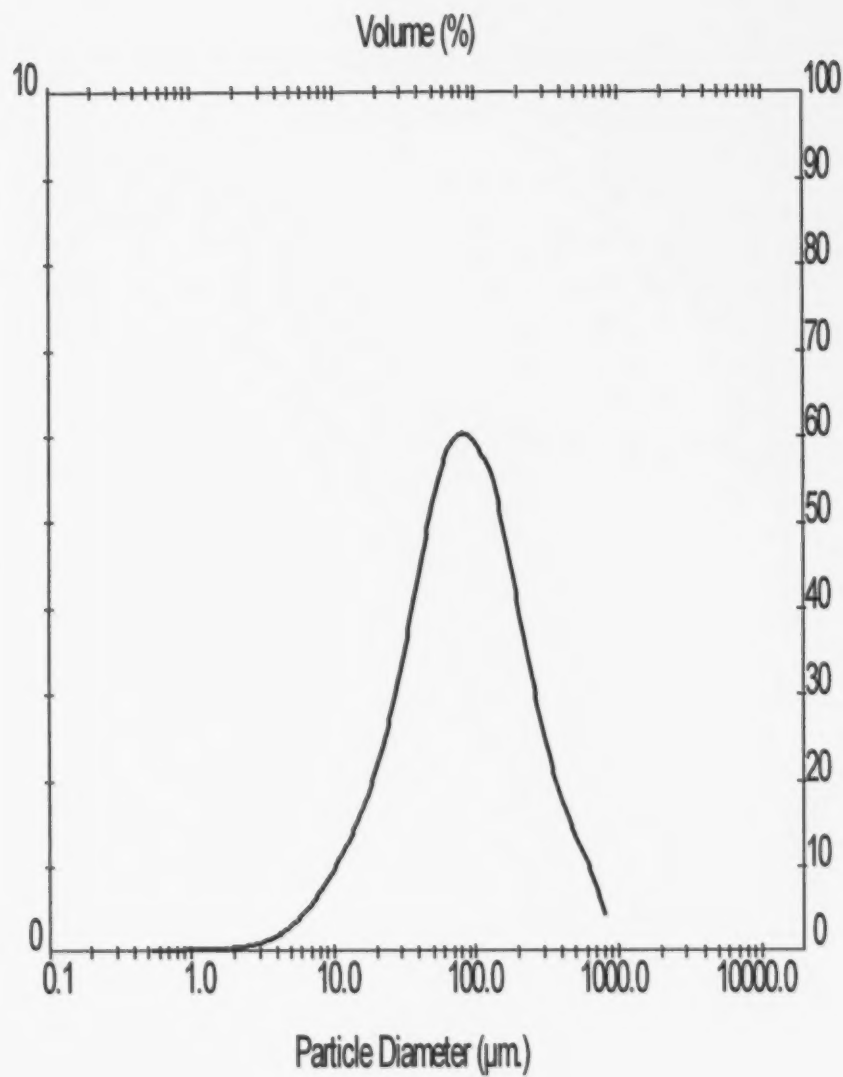
Project Requirements	Option 1 - Wheat Straw	Option 2 - Wheat Chaff	Option 3 - Canola Straw	Option 4 - Rye Straw	Option 5 - Barley Straw	Option 6 - Flax Straw	Option 7 - Hay	Degree of Importance to the Project (1 to 10)	Satisfaction with Current Offering (1 to 10)	Overall Priority (Importance/(Current Offering))	Relative Importance (%)
Low Value of Feedstock	3	5	5	5	3	6	3	6	5	1.2	9
High Volume of Feedstock Produced	9	8	5	3	4	1	4	5	5	0.6	4
Disposal Difficulty/Cost of Feedstock	2	2	2	2	2	6	1	8	5	1.6	14
Environmental Concerns of Feedstock	1	1	1	1	1	3	1	5	5	1.0	7
Market for Technology if Feedstock Selected	4		2	2	2	3	2	8	5	1.6	18
Fit to Technology	5	8	5	5	5	3	6	8	5	1.6	12
Feedstock Collection	5	6	4	4	4	5	4	3	5	0.6	10
Public Perception	3	3	3	2	2	6	1	4	5	0.8	6
Additional Preprocessing requirements (grinding, drying, special handling, leaching etc.)	6	8	6	6	6	4	7	6	5	1.2	9

Potential for High-value End-Use - Oil	3	3	3	3	3	3	3	8	5	1.6	12
Potential for High-value End-Use - Char	3	3	3	3	3	3	3	8	5	1.6	12
Requirement Weight	428	434	382	367	354	448	355	5957			
Relative weight (%)	7.2	7.3	6.4	6.2	5.9	7.5	6.0	100			

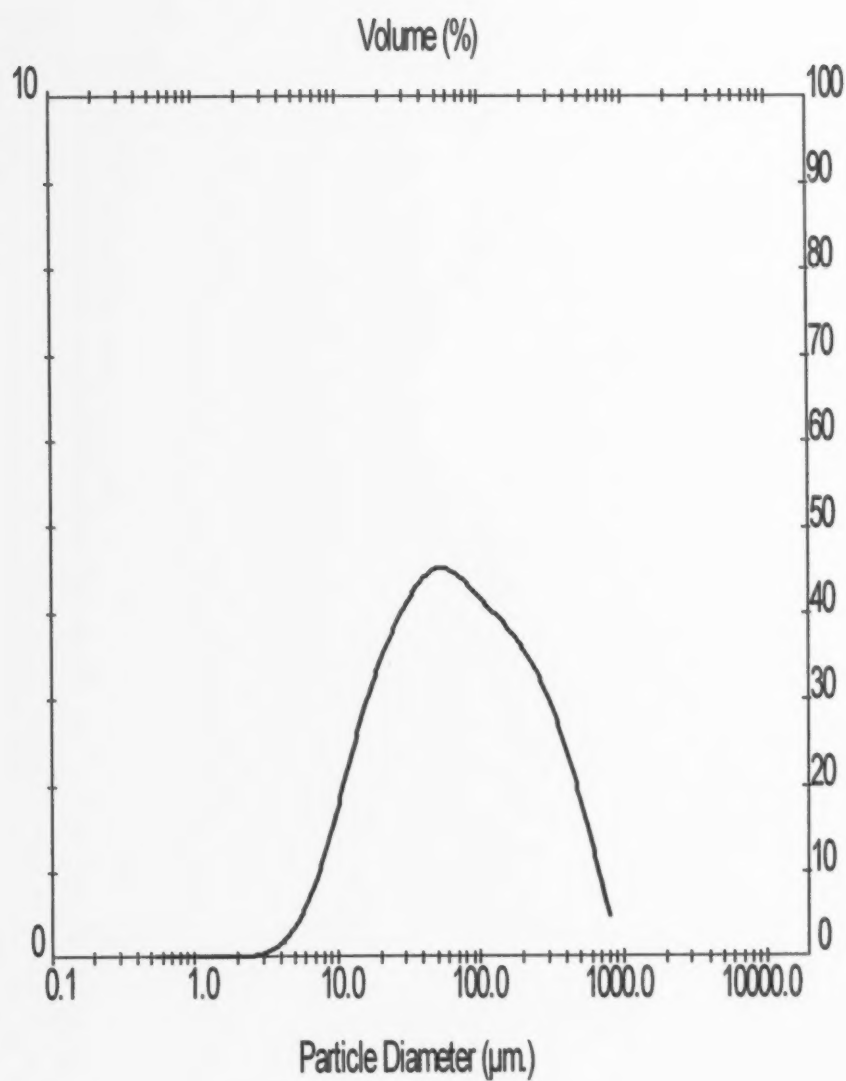
C3: Prioritization Matrix for All Feedstocks under Consideration – Part 2

Project Requirements	Option 8- Hog Manure	Option 9 – Dairy Manure	Option 10 – Beef Cattle Manure	Option 11 – Poultry Litter	Option 12 – Oat Hulls	Option 13 - DDGS	Option 14 – Canola Meal	Degree of Importance to the Project (1 to 10)	Satisfaction with Current Offering (1 to 10)	Overall Priority (Importance/(Current Offering))	Relative Importance (%)
Low Value of Feedstock	5	4	3	7	8	2	2	6	5	1.2	9
High Volume of Feedstock Produced	3	3	9	5	1	3	3	5	5	0.6	4
Disposal Difficulty/Cost of Feedstock	7	5	5	7	5	2	2	8	5	1.6	14
Environmental Concerns of Feedstock	7	3	3	5	1	1	1	5	5	1.0	7
Market for Technology if Feedstock Selected	2	2	2	5	2	4	2	8	5	1.6	18
Fit to Technology	2	2	3	4	7	8	2	8	5	1.6	12
Feedstock Collection	2	2	2	8	6	9	7	3	5	0.6	10
Public Perception	8	7	7	8	3	1	1	4	5	0.8	6

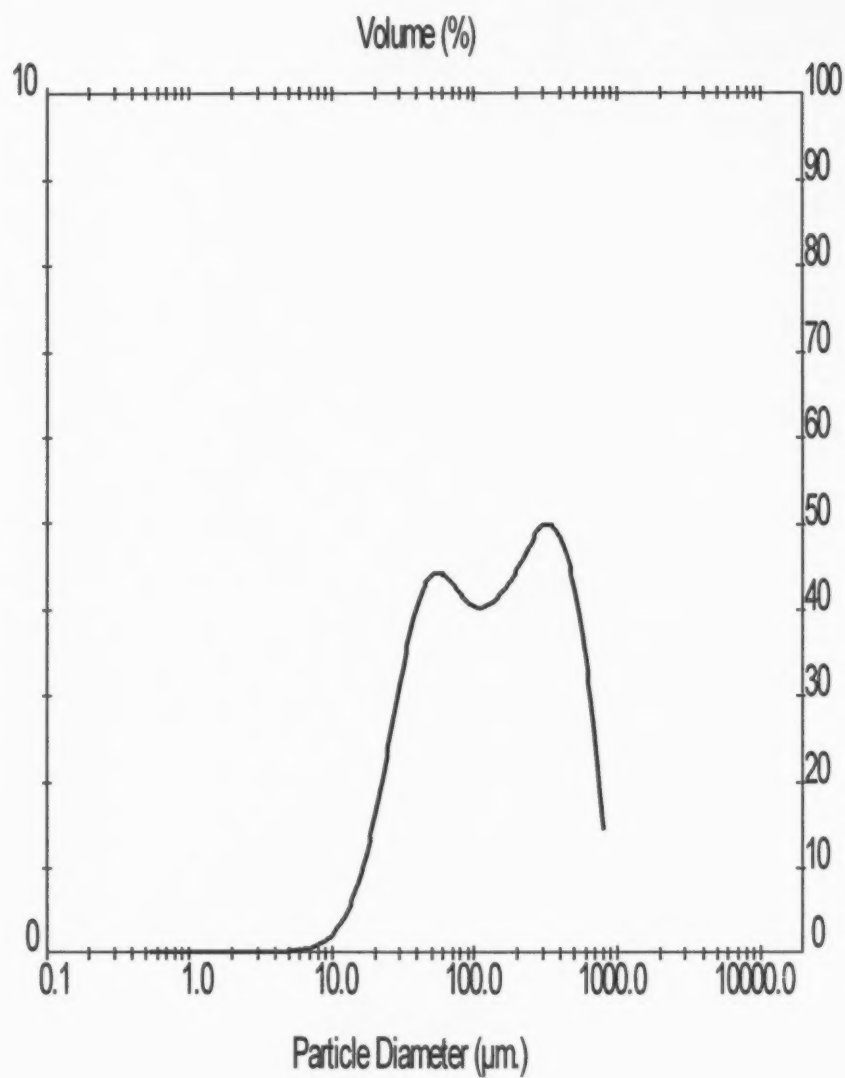
Additional Preprocessing requirements (grinding, drying, special handling, leaching etc.)	2	2	3	4	9	9	9	6	5	1.2	9
Potential for High-value End- Use - Oil	3	3	3	3	3	4	3	8	5	1.6	12
Potential for High-value End- Use - Char	3	3	3	3	7	5	3	8	5	1.6	12
Requirement Weight	424	352	391	594	552	520	356	5957			
Relative weight (%)	7.1	5.9	6.6	10.0	9.3	8.7	6.0	100			

D. Particle Size Analyses

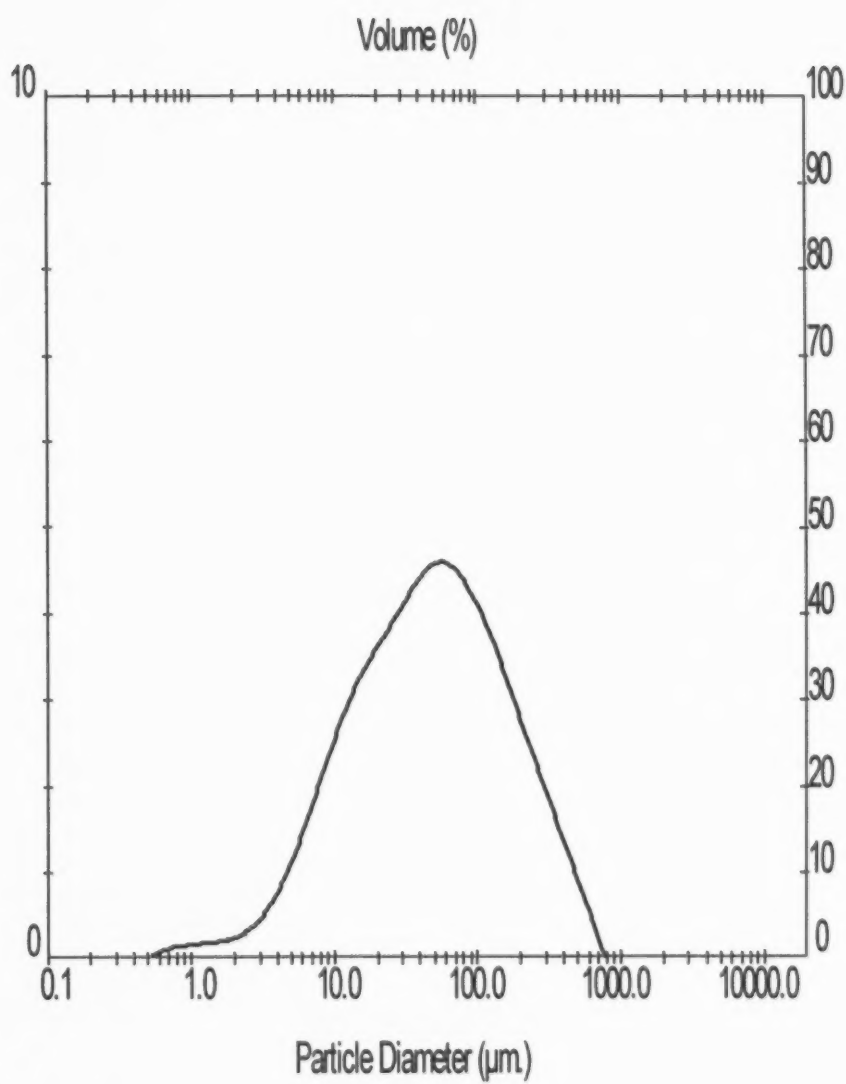
D.1: Particle Size Distribution for Char from Mixed Hardwood Sawdust (Baseline) at 400°C.



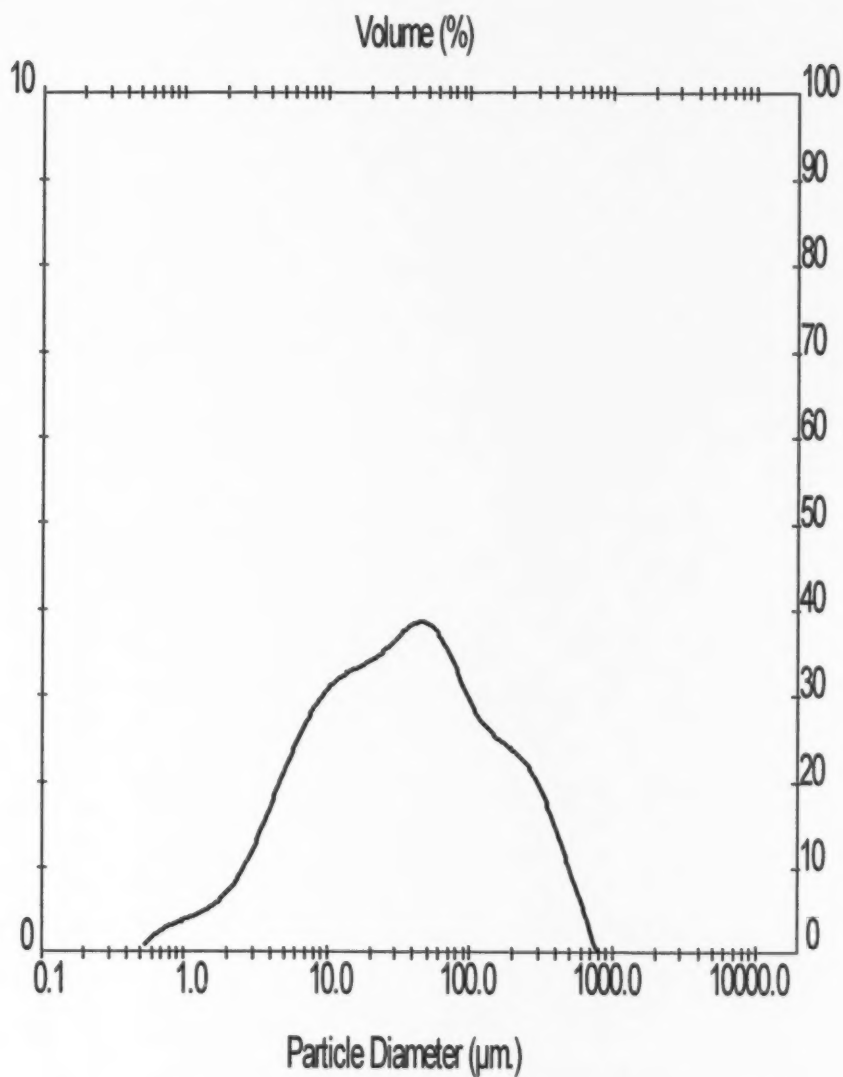
D.2: Particle Size Distribution for Char from Mixed Hardwood Sawdust (Baseline) at 475°C.



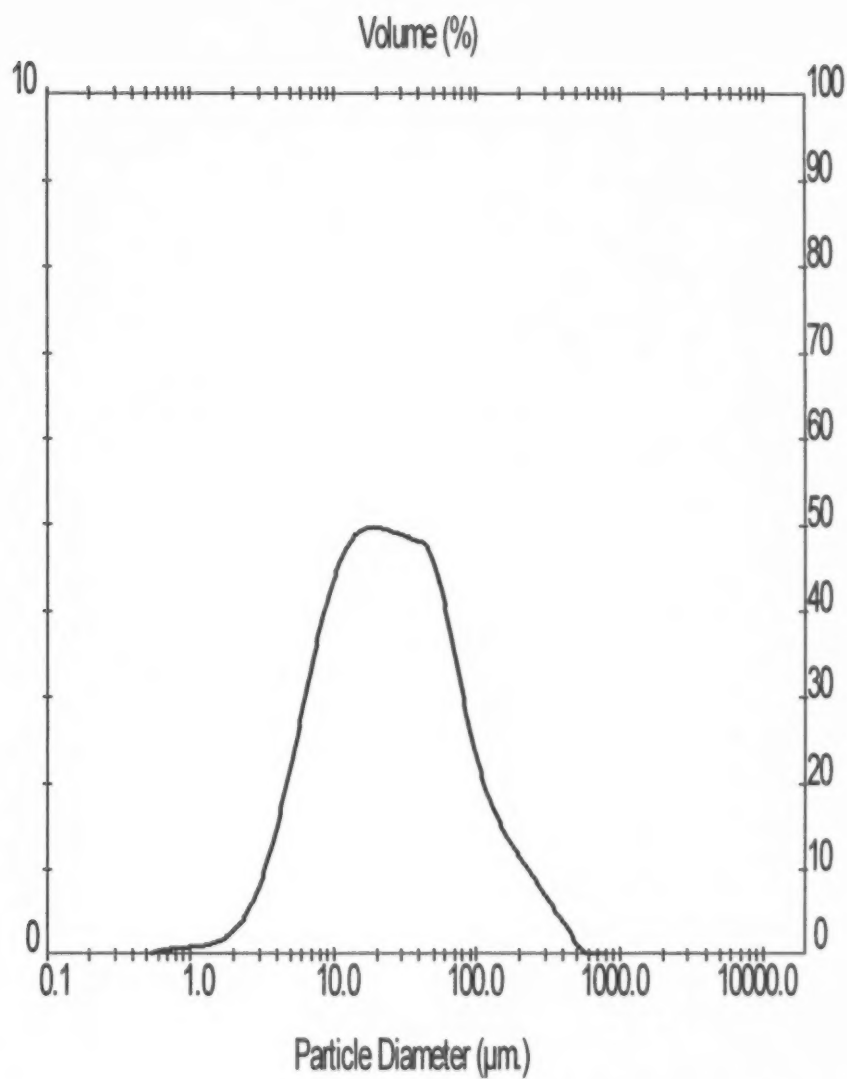
D.3: Particle Size Distribution for Char from Mixed Hardwood Sawdust (Baseline) at 550°C.



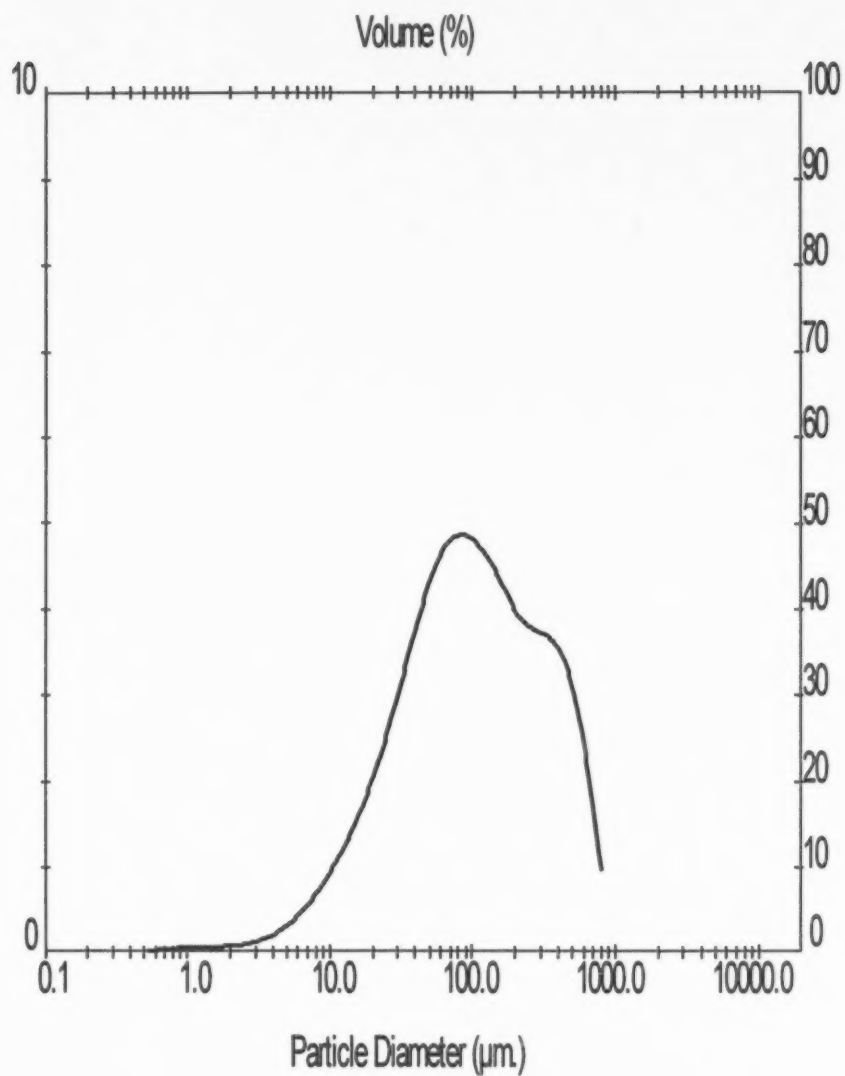
D.4: Particle Size Distribution for Char from Wheat Straw at 400°C.



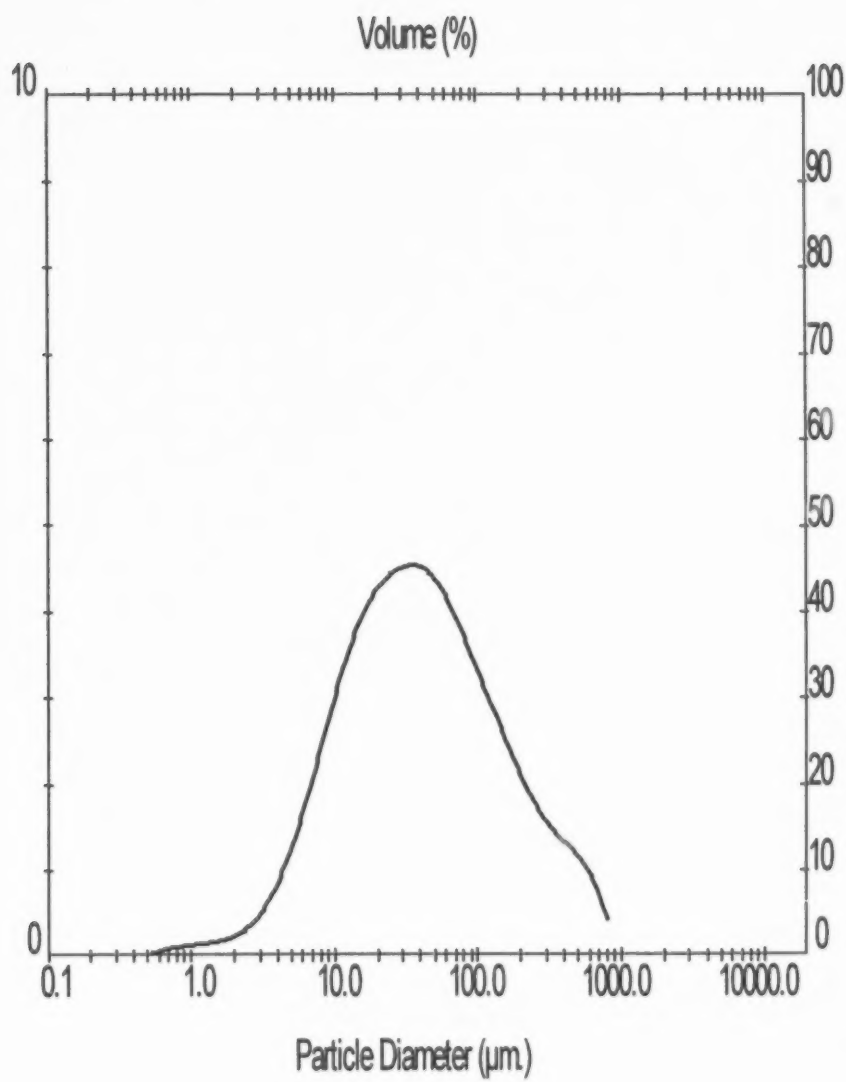
D.5: Particle Size Distribution for Char from Wheat Straw at 475°C.



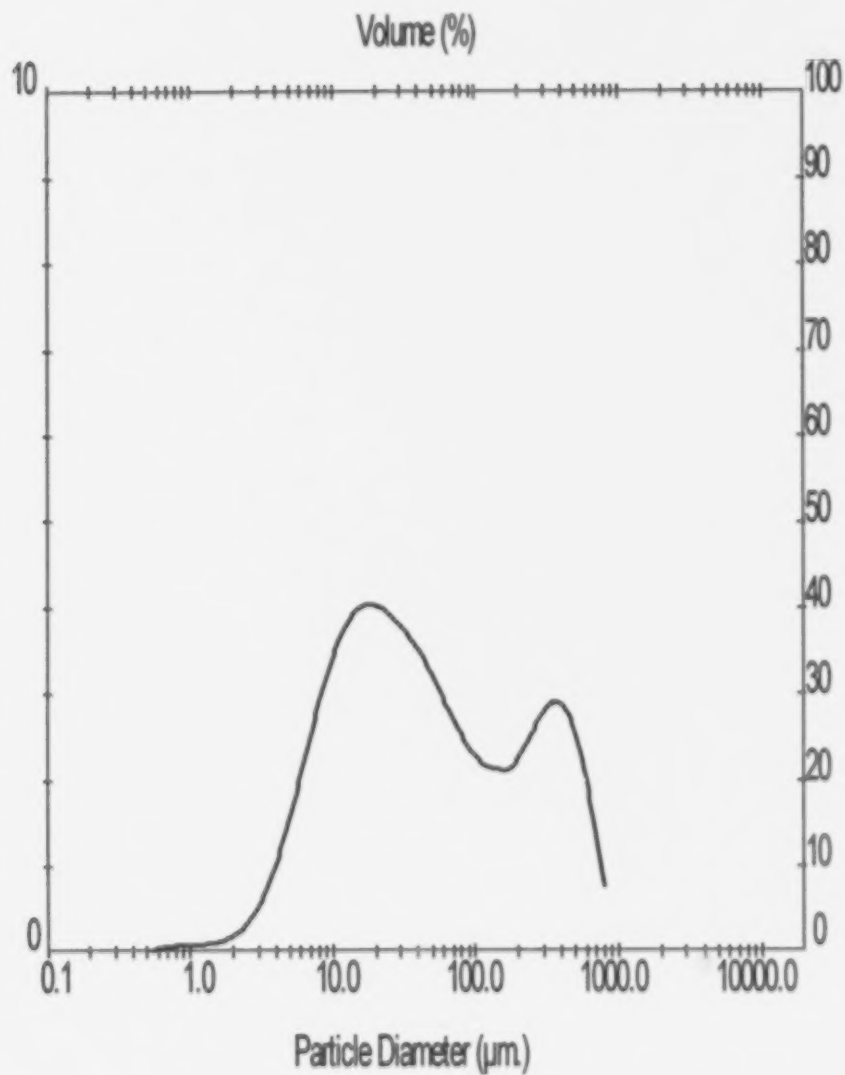
D.6: Particle Size Distribution for Char from Wheat Straw at 550°C.



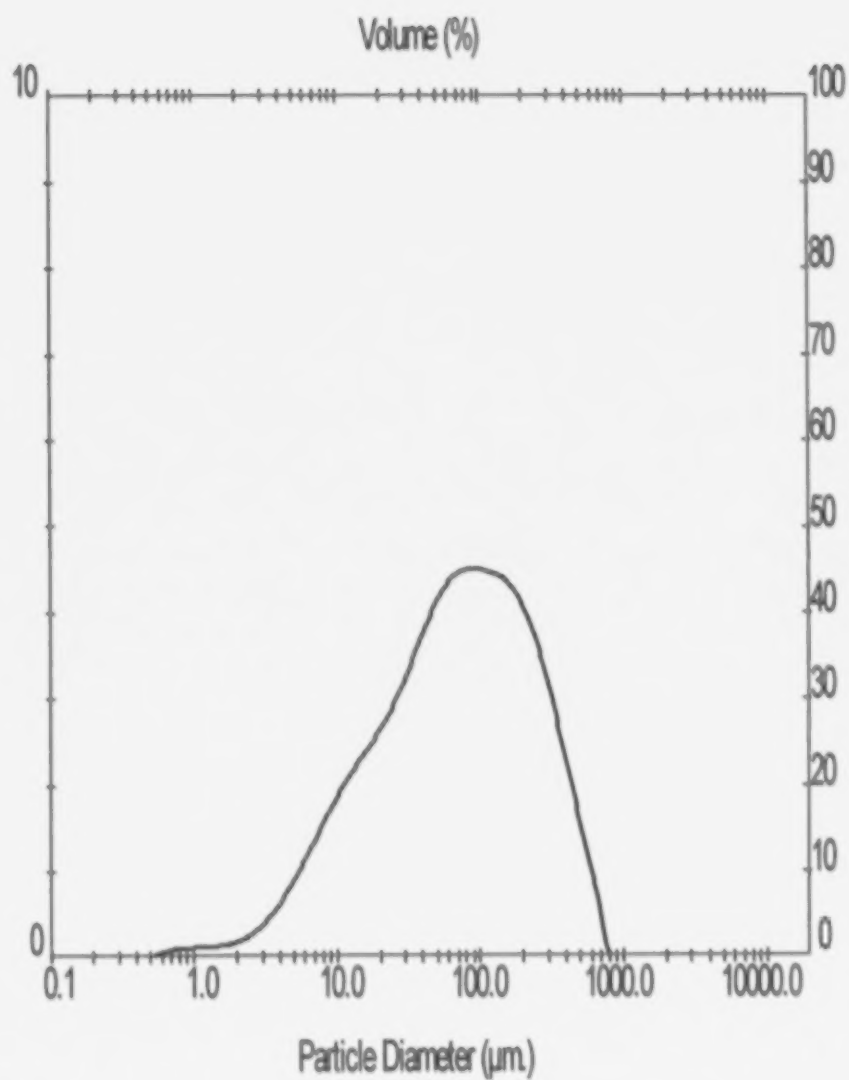
D.7: Particle Size Distribution for Char from Poultry Litter at 400°C



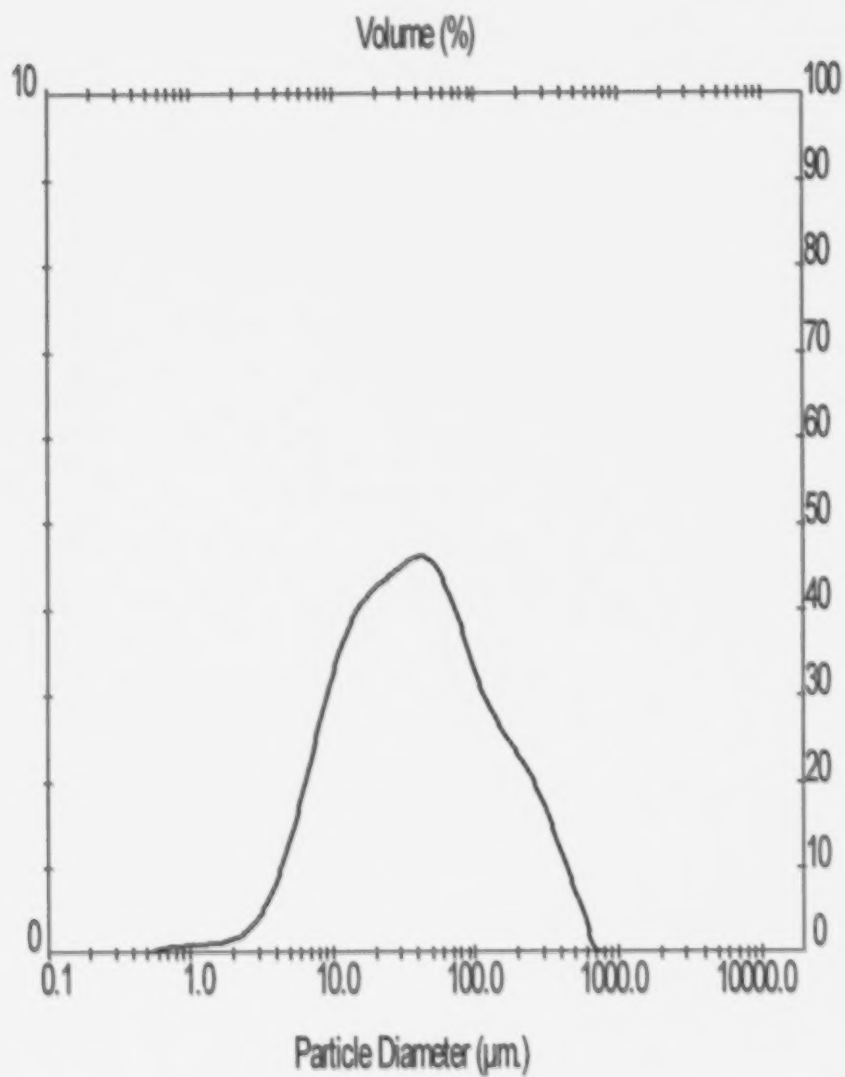
D.8: Particle Size Distribution for Char from Poultry Litter at 475°C.



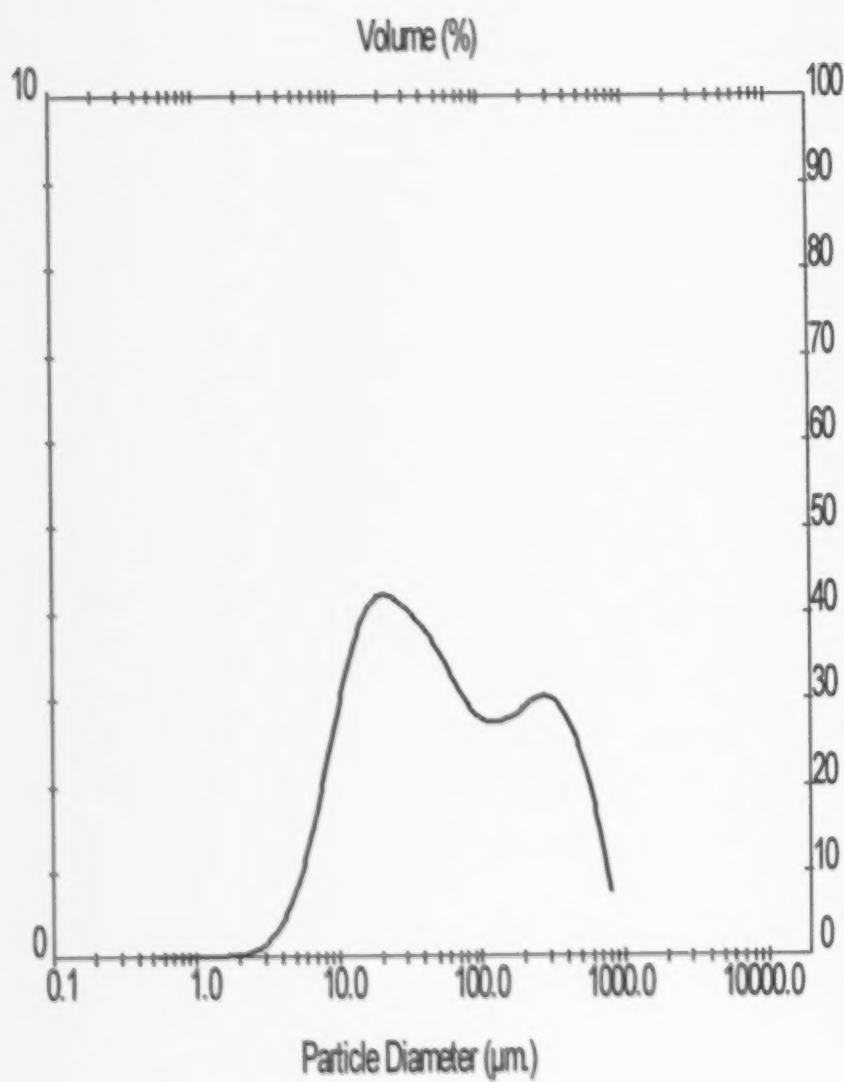
D.9: Particle Size Distribution for Char from Poultry Litter at 550°C



D.10: Particle Size Distribution for Char from Flax Shive at 400°C.



D.11: Particle Size Distribution for Char from Flax Shive at 475°C.



D.12: Particle Size Distribution for Char from Flax Shive at 550°C.

E. Detailed Oil Composition by GC/MS**E.1: Compounds Identified in Oil from Mixed Hardwood Sawdust (Baseline) Pyrolyzed at 400°C.**

Compound	Fraction 1* (wt% of Total)
<u>Phenols:</u>	
naphtalene, decahydro-, trans-	0.36
Naphtalene, 1,2,3,4-tetrahydro-	1.11
Phenol, 2,6-dimethoxy	0.32
1,2,4-trimethoxybenzene	0.46
Phenol, 2-methoxy-4-(1-propenyl)	3.91
Benzene, 1,2,3-trimethoxy-5-methyl-	3.37
phenol, 2,6-dimethoxy-4-(2-propenyl)	17.96
<u>Ketones:</u>	
Ethanone 1-(4-hydroxy-3-methoxyphenyl)-	13.07
2-propanone, 1-(4-hydroxy-3-methoxyphenyl)	1.20
ethanone	0.54
<u>Alcohols:</u>	
1,3-Benzenediol	1.51
1,2-benzenediol, 3-methyl	0.55
Eugenol	1.11
<u>Acids:</u>	
2,4-Hexadienedioic acid, 3,4-diethyl-, dim ethyl ester	0.70
<u>Other Compounds:</u>	
9-methylbicyclo[3.3.1]nonane	0.37
Trisiloxane, octamethyl	0.73

* single oil fraction

E.2: Compounds Identified in Oil from Mixed Hardwood Sawdust (Baseline) Pyrolyzed at 475°C.

Compound	Fraction 1 (wt% of Total)	Fraction 2 (wt% of Total)
<u>Phenols:</u>		
Naphtalene, 1,2,3,4-tetrahydro-	1.12	2.77
phenol, 4-ethyl-2-methoxy	5.21	1.80
Phenol, 2-methoxy-4-(1-propenyl)	45.07	1.50
1,2,4-trimethoxybenzene	2.32	0.94
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	1.62	2.53
benzene, 1,3-dimethyl-		0.47
naphthalene, decahydro-, trans-		0.20
Phenol, 2,6, dimethoxy		1.13
<u>Ketones:</u>		
Ethanone 1-(4-hydroxy-3-methoxyphenyl)-	1.78	3.89
2-propanone, 1-(4-hydroxy-3-methoxyphenyl)		0.89
ethanone, 1-(4-hydroxy-3, 5-dimethoxyphenyl)-		0.70
1-Butanone, 1-(2,4,6-trihydroxy-3-methylphenyl)-		0.59
<u>Alcohols:</u>		
1,3-Benzenediol		2.40
1,2-benzenediol, 3-methyl	3.53	3.50
<u>Acids:</u>		
benzoic acid, 4-ethoxy-, ethyl ester		0.57
<u>Aldehydes:</u>		
Benzaldehyde, 4-hydroxy-3, 5-dimethoxy-		5.58
<u>Other Compounds:</u>		
9-methylbicyclo[3.3.1]nonane	2.74	0.83
Ethane, 1,1,2,2-tetrachloro		0.67

E.3: Compounds Identified in Oil from Mixed Hardwood Sawdust (Baseline) Pyrolyzed at 550°C.

Compound	Fraction 1 (wt% of Total)	Fraction 2 (wt% of Total)
<u>Phenols:</u>		
Naphtalene, 1,2,3,4-tetrahydro-	0.27	1.48
phenol, 4-ethyl-2-methoxy	5.44	1.63
Phenol, 2-methoxy-4-(1-propenyl)	24.22	
1,2,4-trimethoxybenzene	15.68	
Phenol, 2-methoxy-4-propyl		3.14
naphthalene, decahydro-,trans-		23.04
Phenol, 2,6, dimethoxy	0.25	
<u>Ketones:</u>		
Ethanone 1-(4-hydroxy-3-methoxyphenyl)-		0.57
<u>Alcohols:</u>		
Eugenol	1.05	2.66
<u>Other Compounds:</u>		
9-methylbicyclo[3.3.1]nonane		12.38

E.4: Compounds Identified in Oil from Wheat Straw Pyrolyzed at 400°C.

Compound	Fraction 1 (wt% of Total)	Fraction 2 (wt% of Total)
<u>Phenols:</u>		
Phenol (C ₆ H ₆ O)	2.8	
Phenol, 4-ethyl- (C ₈ H ₁₀ O)	2.1	
Phenol, 2-methoxy-4-methyl (C ₈ H ₁₀ O ₂)	1.7	
Phenol, 4-ethyl-2-methoxy (C ₉ H ₁₂ O ₂)	2.7	2.7
2-Methoxy-4-vinylphenol (C ₉ H ₁₀ O ₂)	7.4	27.9
Phenol, 2,6-dimethoxy (C ₈ H ₁₀ O ₃)		4.9
Phenol, 2,6-dimethoxy-4-(2-propenyl)- (C ₁₁ H ₁₄ O ₃)	1.3	3.1
<u>Ketones:</u>		
2-cyclopenten-1-one (C ₅ H ₆ O)	8.1	
Ethanone, 1,2-di-2-furanyl-2-hydroxy (C ₁₀ H ₈ O ₄)	1.8	
2-Cyclopenten-1-one, 2-methyl- (C ₆ H ₈ O)	5.4	
2-cyclopenten-1-one, 3-methyl- (C ₆ H ₈ O)	1.5	
2-Cyclopenten-1-one, 2,3-dimethyl- (C ₇ H ₁₀ O)	9.7	
2-cyclopenten-1-one, 3-ethyl-2-hydroxy (C ₇ H ₁₀ O ₂)	1.4	
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)- (C ₉ H ₁₀ O ₃)	1.2	4.3
Ethanone, 1-(3,4-dimethoxyphenyl)- (C ₁₀ H ₁₂ O ₃)		4.5
2-pentadecanone, 6,10,14-trimethyl- (C ₁₈ H ₃₆ O)		2.2
<u>Alcohols:</u>		
2-Furanmethanol (C ₅ H ₆ O ₂)	8.8	
<u>Acids:</u>		
Cyclobutanecarboxylic acid, 1-amino- (C ₅ H ₉ NO ₂)	1.6	
Propanoic acid, 2-methyl-, anhydride (C ₈ H ₁₄ O ₃)	6.8	
<u>Aldehydes:</u>		
Benzaldehyde, 4-hydroxy-3,5-dimethoxy- (C ₉ H ₁₀ O ₄)	2	
Benzaldehyde, 3-hydroxy-4-methoxy (C ₈ H ₈ O ₃)		4.7

E.5: Compounds Identified in Oil from Wheat Straw Pyrolyzed at 475°C.

Compound	Fraction 1 (wt% of Total)	Fraction 2 (wt% of Total)
<u>Phenols:</u>		
Phenol, 4-ethyl- (C ₈ H ₁₀ O)	2.5	2.4
Phenol, 2-methoxy-4-methyl (C ₈ H ₁₀ O ₂)	1.1	
Phenol, 4-ethyl-2-methoxy (C ₉ H ₁₂ O ₂)	2.2	1.7
2-Methoxy-4-vinylphenol (C ₉ H ₁₀ O ₂)	4.1	15.6
Phenol, 2,6-dimethoxy (C ₈ H ₁₀ O ₃)		2.2
Phenol, 2,6-dimethoxy-4-(2-propenyl)- (C ₁₁ H ₁₄ O ₃)	1.1	1.6
<u>Ketones:</u>		
2-cyclopenten-1-one (C ₅ H ₆ O)	7.5	
Ethanone, 1,2-di-2-furanyl-2-hydroxy (C ₁₀ H ₈ O ₄)	2.3	
2-Cyclopenten-1-one, 2-methyl- (C ₆ H ₈ O)	4.1	
2-cyclopenten-1-one, 3-methyl- (C ₆ H ₈ O)	1.4	
2-Cyclopenten-1-one, 2,3-dimethyl- (C ₇ H ₁₀ O)	2.4	1.9
2-cyclopenten-1-one, 3-ethyl-2-hydroxy (C ₇ H ₁₀ O ₂)	0.9	
2-Furanone, 2,5-dihydro-3,5-dimethyl (C ₆ H ₈ O ₂)	2.1	
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)- (C ₉ H ₁₀ O ₃)		2.3
2-propanone, 1-(4-hydroxy-3-methoxyphenyl)- (C ₁₀ H ₁₂ O ₃)		1.1
Ethanone, 1-(3,4-dimethoxyphenyl)- (C ₁₀ H ₁₂ O ₃)		2.5
<u>Alcohols:</u>		
2-Furanmethanol (C ₅ H ₆ O ₂)	6.9	
<u>Acids:</u>		
Cyclobutanecarboxylic acid, 1-amino- (C ₅ H ₉ NO ₂)	3.8	
Propanoic acid, 2-methyl-, anhydride (C ₈ H ₁₄ O ₃)	19.8	5.9
<u>Aldehydes:</u>		
Benzaldehyde, 4-hydroxy-3,5-dimethoxy- (C ₉ H ₁₀ O ₄)	1.0	8.6
Benzaldehyde, 3-hydroxy-4-methoxy (C ₈ H ₈ O ₃)		3.5

E.6: Compounds Identified in Oil from Wheat Straw Pyrolyzed at 550°C.

Compound	Fraction 1 (wt% of Total)	Fraction 2 (wt% of Total)
<u>Phenols:</u>		
Phenol, 4-ethyl- (C ₈ H ₁₀ O)	10.8	2.1
Phenol, 4-ethyl-2-methoxy (C ₉ H ₁₂ O ₂)	2.9	
2-Methoxy-4-vinylphenol (C ₉ H ₁₀ O ₂)	2.4	10.0
Phenol, 2,6-dimethoxy (C ₈ H ₁₀ O ₃)		0.9
<u>Ketones:</u>		
2-cyclopenten-1-one (C ₅ H ₆ O)	6.4	
2-Cyclopenten-1-one, 2,3-dimethyl- (C ₇ H ₁₀ O)	4.2	
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)- (C ₉ H ₁₀ O ₃)		1.2
<u>Alcohols:</u>		
2-Furanmethanol (C ₅ H ₆ O ₂)	9.8	
<u>Acids:</u>		
Cyclobutanecarboxylic acid, 1-amino- (C ₅ H ₉ NO ₂)	5.1	
Propanoic acid, 2-methyl-, anhydride (C ₈ H ₁₄ O ₃)	20.3	2.8
<u>Aldehydes:</u>		
Benzaldehyde, 3-methyl (C ₈ H ₈ O))		1.4
Benzaldehyde, 3-hydroxy-4-methoxy (C ₈ H ₈ O ₃)		1.2
Benzaldehyde, 4-hydroxy-3, 5-dimethoxy- (C ₉ H ₁₀ O ₄)		2.9

E.7: Compounds Identified in Oil from Poultry Litter Pyrolyzed at 400°C.

Compound	Fraction 1 (wt% of Total)	Fraction 2 (wt% of Total)
<u>Phenols:</u>		
phenol, 4-methyl (8.56 wt %)		8.56
Benzene, 1-ethyl-3-methyl (9.36 %)		9.36
ethylbenzene (10.91%)	10.91	
Naphtalene, 1,2,3,4-tetrahydro- (3.22 %)	3.22	
Phenol, 2,6-dimethoxy (2.08 %)	2.08	
1,2,4-trimethoxybenzene (3.73 %)	3.73	
<u>Ketones:</u>		
2,5-cyclohexadiene-1, 4-dione		4.6
<u>Alcohols:</u>		
1-Dotriacontanol (6.25%)		6.25
Mequinol (6.30 %)	6.30	
1,2-Benzenediol (2.01 %)	2.01	
<u>Nitrogen Compounds:</u>		
Pyridine, 3-methyl		35.78
Pyrazine	1.61	
3,4-dimethyl(1H)pyrrole	9.34	
<u>Other Compounds:</u>		
2H-Naphtho[1,8-bc]thiophene	3.18	

E.8: Compounds Identified in Oil from Poultry Litter Pyrolyzed at 475°C.

Compound	Fraction 1 (wt% of Total)	Fraction 2 (wt% of Total)
<u>Phenols:</u>		
Naphtalene, decahydro-, trans- (1.26 %)		1.26
phenol, 2-ethyl (0.73 %)	0.36	0.73
Naphtalene (0.86 %)		0.86
phenol, 2,3,6-trimethyl- (5.34 %)		5.34
Phenol, 4-ethyl-3-methyl (1.50 %)		1.50
phenol, 2-methoxy-4-(1-propenyl) (0.82 %)		0.82
phenol, 4,6-di (1,1-dimethylethyl)-2 methyl- (2.02 %)		2.02
phenol, 4-ethyl-2-methoxy	0.82	
phenol, 2,6-dimethoxy (1.68 %)	1.68	
1,2,4-trimethoxybenzene (0.53 %)	0.53	
Benzene, 1,2,3-trimethoxy-5-methyl- (0.65 %)	0.65	
<u>Ketones:</u>		
2,5-cyclohexadiene-1, 4-dione	15.95	
<u>Alcohols:</u>		
13-Heptadecyn-1-ol (1.33 %)		1.33
pyrazolo (alcohol) (0.94 %)		0.94
1-Dotriacontanol (4.42 %)		4.42
Mequinol (0.32 %)	0.32	
1,2-Benzenediol (3.78 %)	3.78	
1,2-Benzenediol, 3-methyl (7.97 %)	7.97	
<u>Acids:</u>		
phosphonic acid (1.76 %)		1.76
cyclopropanebutanoic acid (1.20 %)		1.20
<u>Nitrogen Compounds:</u>		
Pyridine, 3-methyl		3.92

Indolizine (1.50 %)		1.50
1H-Indole, 2-methyl (3.52 %)		3.52
pyrazolo (alcohol) (0.94 %)		0.94
5H-5-methyl-6,7-dihydrocyclopentapyrazine (0.24 %)	0.24	
pyrazine (1.41 %)	1.41	
1H-Benzimidazole (1.20 %)	1.20	
3,4-dimethyl9(H)pyrrole (12.06 %)	12.06	
<u>Other Compounds:</u>		
2H-Naphtho[1,8-bc]thiophene	0.89	

E.9: Compounds Identified in Oil from Poultry Litter Pyrolyzed at 550°C.

Compound	Fraction 1 (wt% of Total)	Fraction 2 (wt% of Total)
<u>Phenols:</u>		
Benzene, 1-ethyl-3-methyl (1.45 %)		1.45
phenol, 2,3-dimethyl (2.03 %)		2.03
phenol, 2,3,6-trimethyl- (5.30 %)		5.20
Phenol, 4-ethyl-3-methyl (1.11 %)		1.11
phenol, 2-methoxy-4-(1-propenyl) (2.68 %)		2.68
phenol, 4,6-di (1,1-dimethylethyl)-2 methyl- (2.17 %)		2.17
ethylbenzene (4.03%)	4.03	
phenol, 4-ethyl-2-methoxy (1.67 %)	1.67	
phenol, 2,6-dimethoxy (2.88 %)	2.88	
1,2,4-trimethoxybenzene (1.14 %)	1.14	
benzene, 1,2,3-trimethoxy-5-methyl (0.68 %)	0.68	
<u>Alcohols:</u>		
13-Heptadecyn-1-ol (1.45 %)		1.45
pyrazolo (alcohol) (1.00 %)		1.00
1-Dotriacontanol (2.02 %)		2.02
Maquinal (5.63 %)	5.63	
1,2-benzenediol (2.17 %)	2.17	
<u>Acids:</u>		
cyclopropanebutanoic acid		3.74
<u>Nitrogen Compounds:</u>		
Pyridine, 3-methyl (5.67 %)		5.67
Indolizine (0.84 %)		0.84
1H-Indole, 2-methyl (3.15 %)		3.15
pyrazolo (alcohol) (1.00 %)		1.00

Hexadecanenitrile (2.98 %)		2.98
5H-cyclopentapyrazine (6.71 %)	6.71	
pyrazine (0.63 %)	0.63	
1H-benzimidazole (1.79 %)	1.79	
3,4-dimethyl(1H)pyrrole (5.68 %)	5.68	
Other Compounds:		
1,3,5,7-cyclooctatetraene (0.76 %)	0.76	
cyclopentane (0.89 %)	0.89	
2H-naphtho[1,8-bc]thiophene (1.99 %)	1.99	

E.10: Compounds Identified in Oil from Flax Shive Pyrolyzed at 400°C.

Compound	Fraction 1 (wt% of Total)	Fraction 2 (wt% of Total)
<u>Phenols:</u>		
Ethylbenzene (0.50 wt %)		0.50
phenol (5.25 %)		5.25
phenol, 2-methyl (15.81 %)		15.81
phenol, 4-methyl (2.21 %)		2.21
Naphthalene, 1,2,3,4-tetrahydro (7.86 %)	7.83	7.86
Phenol, 3-ethyl- (0.92 %)		0.92
phenol, 2-1(1-methylethyl)- (15.55 %)		15.55
phenol, 4-ethyl-2-methoxy- (4.30 %)	8.24	4.30
naphthalene, decahydro-,trans-	7.01	
phenol, 2-methoxy-4-methyl (5.78 %)	5.78	
phenol, 2,6-dimethoxy (2.66 %)	2.66	
phenol, 2-methoxy-4-(1-propenyl)- (4.44 %)	4.44	
<u>Ketones:</u>		
2-cyclopenten-1-one, 2,3-dimethyl (0.88 %)		0.88
<u>Alcohols:</u>		
1,3-Benzenediol, 4-ethyl (2.02 %)		2.02
maquinol (5.73 %)	5.73	
<u>Acids:</u>		
Benzoic acid, 4-ethoxy-, ethyl ester (1.73 %)		1.73
<u>Other Compounds:</u>		
9-methylbicyclo[3.3.1]nonane (6.38 %)	6.38	

E.11: Compounds Identified in Oil from Flax Shive Pyrolyzed at 475°C.

Compound	Fraction 1 (wt% of Total)	Fraction 2 (wt% of Total)
<u>Phenols:</u>		
phenol (2.86 %)	2.86	
phenol, 2-methyl- (18.87 %)	8.17	18.87
phenol, 3,4-dimethyl (6.62 %)		6.62
Naphtalene, 1,2,3,4-tetrahydro (6.50 %)		6.50
phenol, 2-(1-methylethyl)- (12.82 %)	6.12	12.82
phenol, 4-ethyl-2-methoxy (2.27 %)		2.27
phenol, 3-ethyl (9.74 %)	9.74	
<u>Ketones:</u>		
2-cyclopenten-1-one, 2,3-dimethyl		5.58
<u>Alcohols:</u>		
1,3-Benzenediol, 4-ethyl (2.02 %)		2.10
1,2,benzenediol (1.91 %)	1.91	
1,3-benzenediol, 4-ethyl (1.29 %)	1.29	
<u>Other Compounds:</u>		
ethane, 1,1,2,2-tetrachloro (3.47 %)	3.47	

E.12: Compounds Identified in Oil from Flax Shive Pyrolyzed at 550°C.

Compound	Fraction 1 (wt% of Total)	Fraction 2 (wt% of Total)
<u>Phenols:</u>		
phenol (5.25 %)		19.59
phenol, 2-methyl (15.81 %)		27.13
phenol, 4-methyl (2.21 %)		1.13
phenol, 3,4-dimethyl (8.08 %)		8.08
Naphthalene, 1,2,3,4-tetrahydro (7.86 %)	4.29	1.45
Phenol, 3-ethyl- (0.92 %)		0.99
phenol, 2-1(1-methylethyl)- (15.55 %)		4.21
phenol, 4-ethyl-2-methoxy- (4.30 %)	2.50	
phenol, 2-methoxy-4-methyl (5.78 %)	15.24	
phenol, 2,6-dimethoxy (2.66 %)	7.23	
<u>Ketones:</u>		
2-cyclopenten-1-one, 2,3-dimethyl (0.88 %)		9.86
<u>Alcohols:</u>		
1,3-Benzenediol, 4-ethyl (2.02 %)	0.90	2.78
1,2-Benzenediol, 4-methyl (0.52 %)	10.76	0.52

F. Economic Evaluation

F.1: Economic Analysis of Pyrolysis Technology, Base Case

Cash Flow, \$1000

Year	0	1	2	3	4	5	6	7	8	9	10
Capital Commitment \$1000	\$160.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0
Revenue Generated & Replacement SM per annum.		\$65.8	\$65.8	\$65.8	\$65.8	\$65.8	\$65.8	\$65.8	\$65.8	\$65.8	\$65.8
Incremental Operating Cost (Increase) Yr 1-10, or Project Expense, Yr 0	\$0.0	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1
Incremental Savings		\$0.9	\$0.9	\$0.9	\$0.9	\$0.9	\$0.9	\$0.9	\$0.9	\$0.9	\$0.9
EBITDA	\$0.0	\$19.6	\$19.6	\$19.6	\$19.6	\$19.6	\$19.6	\$19.6	\$19.6	\$19.6	\$19.6
Project Capital in yr zero or depreciation in out years	\$160.0	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00
Tax (book) (35%)	\$0.0	\$1.3	\$1.3	\$1.3	\$1.3	\$1.3	\$1.3	\$1.3	\$1.3	\$1.3	\$1.3
Net Income	\$0.0	\$2.3	\$2.3	\$2.3	\$2.3	\$2.3	\$2.3	\$2.3	\$2.3	\$2.3	\$2.3
Total Cash Flow	(\$160.0)	\$18.3	\$18.3	\$18.3	\$18.3	\$18.3	\$18.3	\$18.3	\$18.3	\$18.3	\$18.3
Discounted Cash Flow	(\$160.0)	\$17.0	\$15.7	\$14.6	\$13.5	\$12.5	\$11.6	\$10.7	\$9.9	\$9.2	\$8.5
Payback Period, EOY		NA	NA	NA	NA	NA	NA	NA	NA	9.0	10.0
Cumulative Cash	(\$160)	(\$142)	(\$123)	(\$105)	(\$87)	(\$68)	(\$50)	(\$32)	(\$13)	\$5	\$23
Payback Period		1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	8.7	8.7

IRR	2.6%
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NPV	(\$37.0)
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Payback years	8.7
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NPV/Initial Capital	-0.2
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F.2: Economic Analysis of Impact of Bio-Oil Price (increase by \$0.10 to \$0.85) on Economic Assessment

Cash Flow, \$1000											
Year	0	1	2	3	4	5	6	7	8	9	10
Capital Commitment \$1000	\$160.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0
Revenue Generated & Replacement SM per annum.		\$72.7	\$72.7	\$72.7	\$72.7	\$72.7	\$72.7	\$72.7	\$72.7	\$72.7	\$72.7
Incremental Operating Cost (Increase) Yr 1-10, or Project Expense, Yr 0	\$0.0	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1
Incremental Savings		\$0.9	\$0.9	\$0.9	\$0.9	\$0.9	\$0.9	\$0.9	\$0.9	\$0.9	\$0.9
EBITDA	\$0.0	\$26.6	\$26.6	\$26.6	\$26.6	\$26.6	\$26.6	\$26.6	\$26.6	\$26.6	\$26.6
Project Capital in yr zero or depreciation in out years	\$160.0	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00
Tax (book) (35%)	\$0.0	\$3.7	\$3.7	\$3.7	\$3.7	\$3.7	\$3.7	\$3.7	\$3.7	\$3.7	\$3.7
Net Income	\$0.0	\$6.9	\$6.9	\$6.9	\$6.9	\$6.9	\$6.9	\$6.9	\$6.9	\$6.9	\$6.9
Total Cash Flow	(\$160.0)	\$22.9	\$22.9	\$22.9	\$22.9	\$22.9	\$22.9	\$22.9	\$22.9	\$22.9	\$22.9
Discounted Cash Flow	(\$160.0)	\$21.2	\$19.6	\$18.1	\$16.8	\$15.6	\$14.4	\$13.3	\$12.4	\$11.4	\$10.6
Payback Period, EOY		NA	NA	NA	NA	NA	NA	7.0	8.0	9.0	10.0
Cumulative Cash	(\$160)	(\$137)	(\$114)	(\$91)	(\$69)	(\$46)	(\$23)	\$0	\$23	\$46	\$69
Payback Period		1.0	2.0	3.0	4.0	5.0	6.0	7.0	7.0	7.0	7.0

IRR	7.1%
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NPV	\$0.6
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Payback years	7.0
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NPV/Initial Capital	0.0
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F.3: Economic Analysis of Impact of Char Price (increase by \$0.10 to \$0.40) on Economic Assessment

Cash Flow, \$1000											
Year	0	1	2	3	4	5	6	7	8	9	10
Capital Commitment \$1000	\$160.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0
Revenue Generated & Replacement SM per annum.		\$70.2	\$70.2	\$70.2	\$70.2	\$70.2	\$70.2	\$70.2	\$70.2	\$70.2	\$70.2
Incremental Operating Cost (Increase) Yr 1-10, or Project Expense, Yr 0	\$0.0	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1
Incremental Savings		\$0.9	\$0.9	\$0.9	\$0.9	\$0.9	\$0.9	\$0.9	\$0.9	\$0.9	\$0.9
EBITDA	\$0.0	\$24.1	\$24.1	\$24.1	\$24.1	\$24.1	\$24.1	\$24.1	\$24.1	\$24.1	\$24.1
Project Capital in yr zero or depreciation in out years	\$160.0	\$16.0	\$16.0	\$16.0	\$16.0	\$16.0	\$16.0	\$16.0	\$16.0	\$16.0	\$16.0
Tax (book) (35%)	\$0.0	\$2.8	\$2.8	\$2.8	\$2.8	\$2.8	\$2.8	\$2.8	\$2.8	\$2.8	\$2.8
Net Income	\$0.0	\$5.3	\$5.3	\$5.3	\$5.3	\$5.3	\$5.3	\$5.3	\$5.3	\$5.3	\$5.3
Total Cash Flow	(\$160.0)	\$21.3	\$21.3	\$21.3	\$21.3	\$21.3	\$21.3	\$21.3	\$21.3	\$21.3	\$21.3
Discounted Cash Flow	(\$160.0)	\$19.7	\$18.2	\$16.9	\$15.6	\$14.5	\$13.4	\$12.4	\$11.5	\$10.6	\$9.8
Payback Period, EOY		NA	NA	NA	NA	NA	NA	NA	8.0	9.0	10.0
Cumulative Cash	(\$160.0)	(\$138.7)	(\$117.5)	(\$96.2)	(\$75.0)	(\$53.7)	(\$32.5)	(\$11.2)	\$10.0	\$31.3	\$52.5
Payback Period		1.0	2.0	3.0	4.0	5.0	6.0	7.0	7.5	7.5	7.5

IRR	5.5%
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NPV	(\$12.4)
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Payback years	7.5
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NPV/Initial Capital	-0.1
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F.4: Economic Analysis of Impact of Carbon Offset Price (increased to \$180) on Economic Assessment

Cash Flow, \$1000											
Year	0	1	2	3	4	5	6	7	8	9	10
Capital Commitment \$1000	\$160.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0	\$0.0
Revenue Generated & Replacement SM per annum.		\$65.8	\$65.8	\$65.8	\$65.8	\$65.8	\$65.8	\$65.8	\$65.8	\$65.8	\$65.8
Incremental Operating Cost (Increase) Yr 1-10, or Project Expense, Yr 0	\$0.0	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1	\$47.1
Incremental Savings		\$8.1	\$8.1	\$8.1	\$8.1	\$8.1	\$8.1	\$8.1	\$8.1	\$8.1	\$8.1
EBITDA	\$0.0	\$26.8	\$26.8	\$26.8	\$26.8	\$26.8	\$26.8	\$26.8	\$26.8	\$26.8	\$26.8
Project Capital in yr zero or depreciation in out years	\$160.0	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00	\$16.00
Tax (book) (35%)	\$0.0	\$3.8	\$3.8	\$3.8	\$3.8	\$3.8	\$3.8	\$3.8	\$3.8	\$3.8	\$3.8
Net Income	\$0.0	\$7.0	\$7.0	\$7.0	\$7.0	\$7.0	\$7.0	\$7.0	\$7.0	\$7.0	\$7.0
Total Cash Flow	(\$160.0)	\$23.0	\$23.0	\$23.0	\$23.0	\$23.0	\$23.0	\$23.0	\$23.0	\$23.0	\$23.0
Discounted Cash Flow	(\$160.0)	\$21.3	\$19.7	\$18.3	\$16.9	\$15.7	\$14.5	\$13.4	\$12.4	\$11.5	\$10.7
Payback Period, EOY		NA	NA	NA	NA	NA	NA	7.0	8.0	9.0	10.0
Cumulative Cash	(\$160)	(\$137)	(\$114)	(\$91)	(\$68)	(\$45)	(\$22)	\$1	\$24	\$47	\$70
Payback Period		1.0	2.0	3.0	4.0	5.0	6.0	7.0	7.0	7.0	7.0

IRR	7.2%
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NPV	\$5.0
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Payback years	7.0
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NPV/Initial Capital	0.0
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